CHEMICAL APPLICATIONS OF INFRARED LASER PHOTOCHEMISTRY

Thesis by

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ABSTRACT

Infrared multiphoton electron detachment reactions of gas phase carbanions are investigated using the techniques of ion cyclotron resonance spectroscopy. Ions are spatially confined in a low pressure environment for up to several seconds during irradiation with the unfocused output of a line tunable continuous wave CO_2 laser. Analysis of the photodetachment yields as a function of irradiation time, neutral gas pressure, laser intensity and laser wavelength have revealed details of the multiphoton excitation process as well as radiative and collisional relaxation mechanisms. The emphasis for many of these studies is on the wavelength dependence of multiphoton electron detachment yields since the resulting infrared spectra are sensitive probes of molecular structure for distinguishing and identifying isomeric anions. An introduction to low power infrared photochemistry of ions is given in Chapter I.

In Chapter II this technique is used to obtain infrared multiphoton electron detachment spectra of two $C_7H_7^-$ isomers, benzyl and cycloheptatrienyl anions. In the first known example where infrared spectra have been used to probe mechanistic details of an ion-molecule reaction, deprotonation of norbornadiene by CH_3O^- is shown to yield a mixture of benzyl and cycloheptatrienyl anions.

A closer examination of multiphoton electron detachment kinetics is the subject of Chapter III. The results are interpreted in terms of a

kinetic model which is developed to describe low power multiphoton excitation and vibrational relaxation. Radiative relaxation of benzyl anion does not appear to be significant at laser intensities greater than 10 W/cm^2 and collisions with neutral molecules are only moderately effective in deactiviating vibrationally excited anions.

Identification of cis and trans butenyl anions in Chapter IV demonstrates the sensitivity of this technique for differentiating molecular structures. Deprotonation of cis-2-butene by NH_2^- forms the cis anion while deprotonation of trans-2-butene results in a mixture of cis and trans $C_4H_7^-$. The multiphoton electron detachment spectrum of a third isomer, 2-methylallyl anion, is also presented.

Vibrational relaxation of allyl anion, $C_3H_5^-$ is probed by infrared laser photodetachment techniques in Chapter V. In contrast to the results for benzyl anion in Chapter III, the radiative relaxation of 53 s^{-1} for allyl anion shows this to be the dominant mechanism for relaxation at pressures below 10^{-5} torr.

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CHAPTER I

Introduction

Since the development of very high power pulsed lasers, and in particular the CO_2 TEA laser, a burgeoning body of literature has been devoted to understanding the mechanism by which the absorption of many photons initiates chemical reactions. Most of these studies have dealt with small polyatomic molecules in static gas cells or molecular beams. Although many different applications of infrared laser chemistry have been explored, most research efforts in this field have centered about two goals. The separation or enrichment of rare isotopes depends on the ability of the laser to selectively induce a chemical reaction in molecules containing a particular isotope at the expense of molecules containing one or more other isotopes. This type of molecular selectivity has been demonstrated in a number of cases and in at least one case, laser isotope separation has been shown to be economically feasible on an industrial scale.[1] The other major goal has been to demonstrate a vibrational mode specificity in which the properties of the laser can be used to control the photochemical mechanism. Results in this area have been mostly disappointing and although some workers have claimed to have observed mode dependent reactions,[2] it is now generally believed that vibrational energy flow within molecules is fast compared with photon absorption or unimolecular reaction rates.[3] As a result, any particular molecule will undergo the same reactions whether it is excited photolytically by expensive laser photons or thermally by a hot wire costing a few cents.

During the past several years much progress has been made in understanding the mechanism of multiphoton excitation using pulsed infrared lasers. At low energies, absorption occurs resonantly so that

three to five quanta are deposited in a particular vibrational mode. Intramolecular vibrational relaxation then channels the energy into other modes which act as a heat bath for vibrational energy storage. At this level of excitation (8-15 kcal/mol) the density of vibrational states in polyatomic molecules is often quite high (>100 states per cm^{-1}). Energy transfer to the molecular heat bath may often occur without the need of a collision to accept the difference in energy between the state pumped and the accepting state of the heat bath. Non-resonant absorption in this quasi-continuum of vibrational states then continues until the molecule contains sufficient energy to undergo chemical change, which usually takes the form of unimolecular dissociation or isomerization. Specific details of the process vary from case to case, but this basic theme is believed to describe infared multiphoton excitation in many molecules when pulsed lasers are used.[4]

No attempt will be made here to give a detailed review of pulsed laser infrared photochemistry. The interested reader is referred to several recent reviews of the subject.[5] Two developments in this field, however, had a significant bearing on the development of low power cw (continuous wave) infrared photochemistry of ions which is the subject of this thesis. The first was a report by Bloembergen and co-workers that infrared multiphoton dissociation (MPD) of SF_6 is dependent not on the intensity of the laser pulse, but only on the fluence, or total energy of the pulse divided by the beam area.[6] Furthermore, it was reported that multiphoton dissociation of SF_6 exhibits a fluence threshold. Assuming that this claim is valid over a wide range of laser intensities and irradiation times suggests the possibility of dissociating

a molecule with laser powers of only a few watts per square centimeter by irradiating for one second, a remarkable supposition! To be successful, the molecule would have to be contained in a collisionless environment to avoid collisional deactivation of the vibrationally excited intermediate. The importance of laser intensity effects has since been recognized by many researchers,[4] but this report stands as one of the major cornerstones on which cw infrared laser photochemistry of ions was founded.

The second major development was the observation that very large molecules can be dissociated using low power CO_2 laser excitation.[7] Volatile uranyl complexes such as UO_2(hexafluoroacetylacetonate)$_2 \cdot$ THF have enough ordinary thermal energy in their vibrational degrees of freedom that they are already in the so-called vibrational quasi-continuum at room temperature. Sufficient numbers of infrared photons may be absorbed non-resonantly to cause dissociation. In this respect, multiphoton dissociation in the large molecular limit embodies many of the same features as dissociation of smaller molecules in the long time (low power) limit.

Both of these characteristics, fluence dependent MPD yields and non-resonant excitation of large molecules, were combined in the first report of cw infrared laser dissociation of ions by Woodin, Bomse and Beauchamp.[8] Ion cyclotron resonance (ICR) spectrometry was used to spatially confine the proton bound dimer of diethyl ether, $[(C_2H_5)_2O]_2H^+$, at 10^{-6} torr for up to several seconds. Irradiation with the unfocused output of a cw CO_2 laser at 2 W/cm^2 resulted in loss of one ether molecule, leaving $(C_2H_5)_2OH^+$.

Several reports since then have characterized this phenomenon under various conditions using different molecular ions,and a general scheme for describing low power multiphoton excitation has been developed.[9] In all but a few cases, photodestruction of a population of ions exhibits an exponential time dependence. This permits a convenient description of the overall multiphoton dissociation process as a first-order unimolecular reaction. Moreover, the dependence of the photodissociation rate on laser intensity is usually linear so that a phenomenological cross section can be defined. This is just the photodissociation rate constant (obtained from the exponential decay) divided by the laser photon flux.

As expected, increasing the pressure of neutrals in the ICR cell results in a decrease in the dissociation rate of large molecules. For smaller molecules, however, collisional enhancement of dissociation rates has been observed.[9] It is thought that this effect is manifested in the increased rates of energy transfer out of the "pumped" vibrational mode and into the molecular heat bath. This effect is probably most important at low overall levels of excitation where the low density of vibrational states can cause significant energy mismatches between the pumped state and the accepting states of the heat bath.

Various methods of preparing ions in excited states can enable an ion to undergo multiphoton dissociation when excitation from the ground state does not occur. Trifluoromethyliodide cation, for example, only dissociates from the $^2E_{\frac{1}{2}}$ excited electronic state which is populated by electron impact formation of CF_3I^+.[10] In another instance, vibrationally excited cyanobenzene cation was prepared by electronic excitation

followed by internal conversion. Infrared laser dissociation occurs from these excited levels, but not from the ground state.[11]

In every case where infrared photochemistry is observed, variation of the laser wavelength while keeping all other conditions the same produces a photodissociation spectrum of the ion. How is this spectrum related to the infrared absorption spectrum? No definitive answer to this question is possible yet, since true absorption spectra are extremely difficult to obtain for ions. In the few instances where absorption spectra have been obtained,[12] the ions have been too small to observe dissociation with a cw CO_2 laser. The limited available evidence which addresses this question seems to indicate that low power dissociation spectra and absorption spectra are similar. The position and lineshape of the $C_3F_6^+$ dissociation spectrum is quite similar to a band in the absorption spectrum of neutral C_3F_6.[9] Furthermore, in the large molecule limit for neutrals, the dissociation spectra of large uranyl compounds exactly match the absorption spectra obtained by low power photoacoustic measurements.[13] For smaller neutrals such as SF_6, a distinct red shift of the photodissociation spectrum is observed relative to the absorption spectrum, but this red shift may be partly or wholly associated with resonant excitation through the sparse, low-lying vibrational levels that is made possible by a high power CO_2 TEA laser.[4]

It is unlikely that the infrared absorption cross section of a vibrationally excited molecule has exactly the same wavelength dependence as that of the ground state. Anharmonic coupling, combination bands and rotational excitation would all tend to broaden an absorption

profile, "smearing out" the oscillator strength over a broader range of frequencies. Transitions between excited levels of vibrational modes would be expected to have increased oscillator strengths in the harmonic approximation. The contribution of these transitions to the overall excitation is expected to be small, however, when the average energy per vibrational mode is low. This is usually the case for moderate sized ions (9-15 atoms) with reasonably low dissociation thresholds ($<$50 kcal/mol).

Despite the fact that absorption profiles may change with increasing vibrational energy, the ground state absorption spectrum governs the probability of absorbing the first photon. It therefore seems likely that the dissociation spectrum will bear a strong resemblance to the absorption spectrum. Whether or not future experiments bear this out, mass spectrometry is likely to play a major role in obtaining the infrared spectra of many different ions by indirect methods such as photodissociation. Detailed high resolution spectra over a wide range of frequencies will allow thorough investigations of molecular structure and bonding in molecular cations and anions.

In this thesis, several aspects of infrared photochemistry of molecular anions are discussed. Studies of anions differ significantly from those of cations in that the lowest energy decomposition pathway is usually electron detachment since electron affinities are most often less than chemical binding energies. Although they are conceptually different in their dissociation mechanisms,[18] kinetic analysis of infrared multiphoton electron detachment (MED) is very similar to that of multiphoton dissociation because both processes are driven by

vibrational photoexcitation. It is doubtful that the dissociation or electron detachment step plays a significant role in determining the overall kinetic behavior since these processes are much faster than photon absorption or vibrational relaxation when low power lasers are used.

In Chapter II, results describing multiphoton electron detachment with a low power infrared laser are described for the first time. Infrared spectra of $C_7H_7^-$ isomers have been obtained using this technique. The spectra are used to identify the product ions obtained from deprotonation of norbornadiene by CH_3O^- as a mixture of benzyl and cycloheptatrienyl anions. This represents the first known instance in which infrared spectra have been used to probe mechanistic details of an ion-molecule reaction in the gas phase.

Chapter III presents a closer examination of multiphoton electron detachment from benzyl and cycloheptatrienyl anions. The effects of varying laser intensity, wavelength, neutral gas pressure and irradiation period are discussed in terms of a kinetic model of sequential multiphoton excitation. The results indicate that the principal mode of vibrational relaxation in this case is collisional energy transfer. Infrared radiative relaxation is thought to play a minor role in deactivating vibrationally excited intermediates.

An examination of infrared MED spectra of butenyl anions is presented in Chapter IV. Cis and trans isomers of $C_4H_7^-$ have been distinguished and identified in the gas phase for the first time using this method. Kinetic analysis of the photodetachment rates, which is only

possible using low power excitation, has been used to full advantage in this case. Quantitative analysis of mixtures of butenyl anion isomers is made possible because cis and trans butenyl anions have very different photodetachment cross sections at 1076 cm^{-1}. Proton transfer reaction of NH_2^- with trans-2-butene is judged to be a poor method of preparing trans-butenyl anion since the major product is the more stable cis isomer. For comparison, the spectrum of a third $C_4H_7^-$ isomer, 2-methylallyl anion, is presented. No interconversion of this isomer with the cis and trans forms was observed.

An analysis of radiative vibrational relaxation in allyl anion is presented in Chapter V. Multiphoton electron detachment is a convenient method of studying relaxation processes in small polyatomic anions because the excitation process is often a sensitive function of vibrational energy. Low power cw excitation is especially suitable for these studies since the possible effects of coherent excitation do not have to be considered. The experimentally determined relaxation rate of 53 s^{-1} is significantly faster than the rate calculated using a simple statistical model. Although radiative relaxation rates are important for modelling radiative association reactions in the interstellar medium, there are very few experimental probes of this process for polyatomic molecules. It is anticipated that this experimental methodology will be used to obtain relaxation rates for other anionic and cationic systems.

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CHAPTER II

Infrared Spectra of Gas Phase Ions and Their Use in Elucidating Reaction Mechanisms. Identification of $C_7H_7^-$ Structural Isomers by Multiphoton Electron Detachment Using a Low Power Infrared Laser.

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Abstract:

Vibrational spectra of benzyl and cycloheptatrienyl anions have been obtained by multiphoton electron detachment using a low power line tunable cw CO_2 laser. The ions are trapped at low pressure using ion cyclotron resonance spectroscopy. Vibrational spectra obtained by monitoring the extent of photodetachment as a function of wavelength have been used to demonstrate that reaction of CH_3O^- with norbornadiene (bicyclo [2. 2. 1] hepta-2, 5-diene) yields both cycloheptatrienyl and benzyl anions in a deprotonation reaction accompanied by isomerization.

The ability to distinguish structural isomers of ions on the basis of their vibrational spectra is of considerable interest since a general method would greatly extend the capabilities of mass spectrometry. It is difficult to achieve number densities of gas phase ions sufficient to observe infrared absorption directly,[1-4] so indirect methods have been developed by inducing unimolecular[5] or modified bimolecular[6] reactivity as a result of absorption of one or more infrared photons. We have explored the technique of multiphoton dissociation using cw and pulsed infrared lasers to obtain spectra of positive ions.[7-10] Multiphoton electron detachment (MED) from negative ions was recently reported by Brauman and coworkers using high power laser pulses from a CO_2-TEA laser.[11] These initial studies have inspired an interesting theoretical treatment of vibrationally induced electron detachment.[12] In this report we present the infrared MED spectra of isomeric $C_7H_7^-$ ions obtained with a low power cw CO_2 laser. This methodology has been used to probe mechanistic details of an ion-molecule reaction in the gas phase for the first time, showing that deprotonation of 2, 5-norbornadiene by CH_3O^- is accompanied by structural rearrangement to benzyl and cycloheptatrienyl anions.

The ion cyclotron resonance spectrometer and optical configuration have previously been described in detail.[13, 14] Briefly, ions are trapped at low pressures, typically 10^{-6} torr, for periods up to several seconds during which they are irradiated with the unfocused output of a line tunable cw CO_2 laser (Apollo Lasers Model 550A). The anions of interest are formed by proton transfer reactions of anionic bases[15] with the neutral C_7H_8 isomers in reactions (1) - (3).

$$CH_3O^- + C_6H_5CH_3 \rightarrow C_6H_5CH_2^- + CH_3OH \quad (1)$$

$$CH_3O^- + \text{cyclo-}C_7H_8 \rightarrow \text{cyclo-}C_7H_7^- + CH_3OH \quad (2)$$

$$NH_2^- + \text{norbornadiene} \rightarrow C_7H_7^- + NH_3 \quad (3)$$

After an initial ion formation period, laser irradiation causes the ion population to decay exponentially in time, with an induction period which is evident at laser intensities less than 20 W/cm^2.[14] Recycling of the detached electrons to form additional $C_7H_7^-$ is prevented by double resonance ejection of the precursor base during the irradiation period.

The electron affinity of benzyl radical is 20 kcal/mol.[16] Therefore, a minimum of eight infrared photons must be absorbed by benzyl anion to reach the electron detachment threshold. Similarly, the electron affinity of cycloheptatrienyl radical is estimated to be 13 kcal/mol[17] so that at least five photons are required for direct electron detachment from the anion. Interestingly, the latter process might not occur directly if the barrier to isomerization from cyclo-$C_7H_7^-$ to $C_6H_5CH_2^-$ is less than 13 kcal/mol. Following structural rearrangement, autodetachment of an electron would be expected because the heat of formation of cycloheptatrienyl anion is greater than that of benzyl radical and a free electron. Unfortunately, the two possible mechanisms may not be distinguished since neutral products are not detected. Further details of the sequential multiple photon excitation process leading to electron detachment will be presented elsewhere.[18]

Infrared spectra of cycloheptatrienyl and benzyl anions are obtained by monitoring the extent of photodetachment as a function of laser wavelength at a fixed intensity and irradiation period (Fig. 1a).

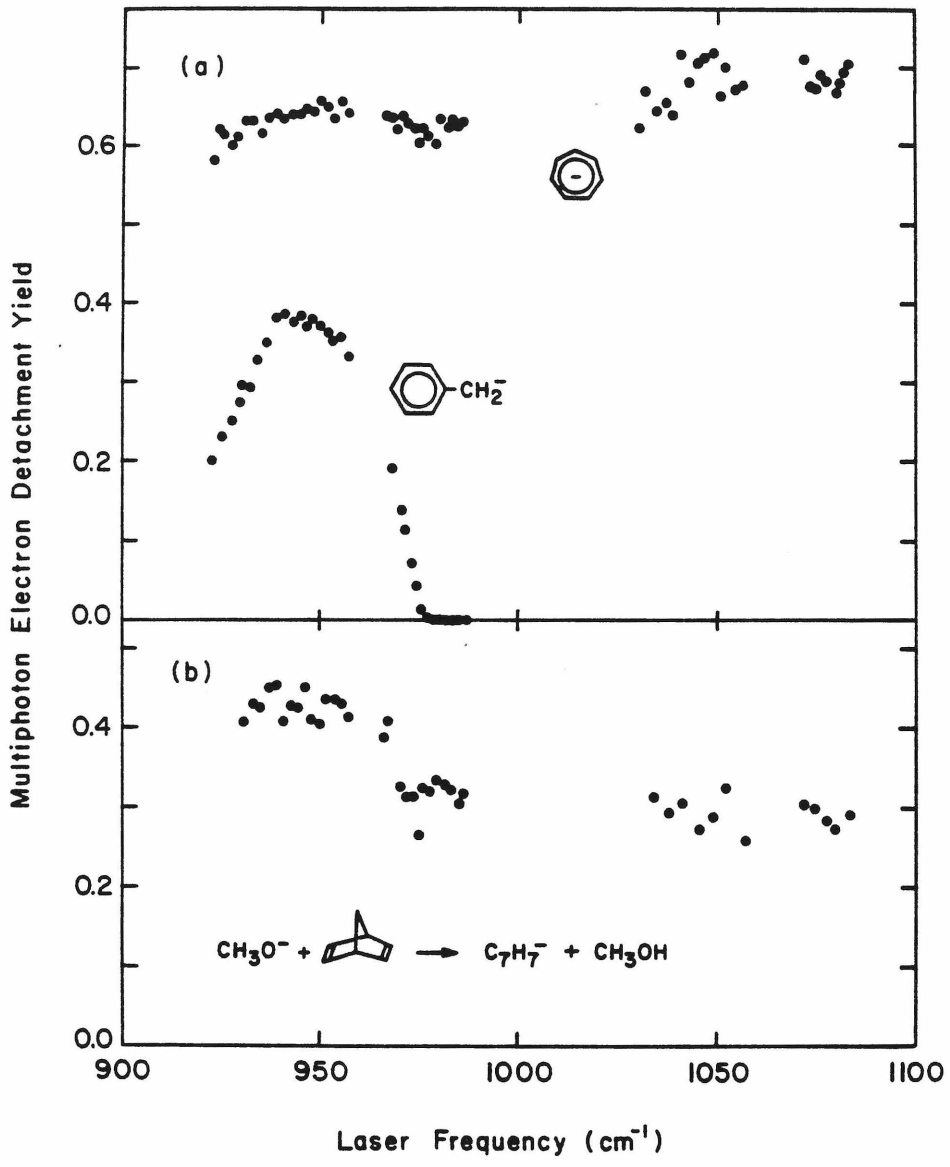
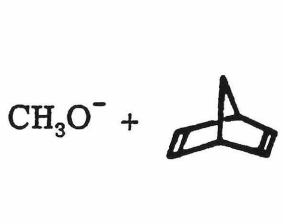


Fig. 1 - Infrared spectra of $C_7H_7^-$ isomers showing multiphoton electron detachment yield vs. laser wavelength. (a) Spectra of cycloheptatrienyl (upper points) and benzyl (lower points) anions. Irradiation was for 200 ms at 24 W/cm^2. MED yield for benzyl anion was zero above 1000 cm^{-1}. (b) Spectrum of cycloheptatrienyl/benzyl mixture formed by deprotonation of norbornadiene by CH_3O^-. Irradiation was for 200 ms at 24 W/cm^2.

Irradiation of $C_7H_7^-$ formed by deprotonation of norbornadiene with NH_2^-, reaction (3), results in no detectable electron detachment, indicating a third distinct $C_7H_7^-$ isomer. There is the possibility that the energy content of the ion influences the probability of multiphoton excitation and electron detachment.[10] This possibility is unlikely in the present case and deuterium isotope exchange reactions in a flowing afterglow[19] support three distinct isomers.

Since three isomers are distinguished by their photodetachment spectra, the above experimental methodology may be used to identify $C_7H_7^-$ anions whose structures are uncertain. Reaction of CH_3O^- with norbornadiene results in cyclopentadienyl anion as the major product, reaction (4), although some $C_7H_7^-$ is produced in reaction (5). Norbornadiene is only weakly acidic,[20] however, and deprotonation analogous



to reaction (3) is endothermic by 23 kcal/mol in this case. Simultaneous structural rearrangement and deprotonation would make reaction (5) exothermic to form benzyl (ΔH_r = -39 kcal/mol) or cycloheptatrienyl (ΔH_r = -12 kcal/mol) anions and these are considered the most likely structures for $C_7H_7^-$ in reaction (5).

When the reaction products are irradiated with the cw CO_2 laser, the spectrum of $C_7H_7^-$ in Fig. 1b is obtained. Although the low resolution of the spectra introduces some uncertainty, the spectrum in Fig. 1b

appears to represent a mixture of cycloheptatrienyl and benzyl anions in a ratio of 1.5:1, respectively.[21] This unusual rearrangement to two different structural isomers has subsequently been observed in a flowing afterglow apparatus for the reaction of hydroxide ions with norbornadiene, yielding benzyl and cycloheptatrienyl anions as products.[22] In the flowing afterglow, structural isomers are distinguished by successive proton exchange reactions with CH_3OD or D_2O.[23]

Multiphoton electron detachment represents a convenient general method for obtaining infrared spectra of negative ions because most photodetachment thresholds lie well below thresholds for photodissociation. In addition, stable negative ions may be formed by proton transfer from an enormous number of molecules with labile protons. With the development of moderately intense (>1 W/cm^2) lasers in other regions of the infrared, more extensive spectra will be obtained yielding detailed information about structure and bonding in molecular ions. With sufficient laser intensities it is anticipated that recording infrared spectra may become a routine application of mass spectrometry.

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20. Norbornadiene is easily deprotonated by NH_2^- but not by H^-, leading to an estimated acidity $D(H^+ - C_7H_7^-) = 402 \pm 5$ kcal/mol.

21. Direct comparison of the yields in Fig. 1(a) and (b) is complicated by the moderately high pressure (5×10^{-6} torr) required to observe reaction (5). The MED yields are empirically corrected for collisional deactivation effects to obtain the reported composition of the $C_7H_7^-$ signal.

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CHAPTER III

Multiphoton Electron Detachment Studies of $C_7H_7^-$ Using a Low Power Infrared Laser. Competition of Radiative and Collisional Relaxation with Vibrational Excitation.

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Abstract:

The techniques of ion cyclotron resonance spectroscopy are used to study infrared laser induced electron detachment of $C_6H_5CH_2^-$, $C_6D_5CD_2^-$ and cyclo-$C_7H_7^-$. Anions are trapped at low pressure for up to several seconds and are uniformly irradiated with the unfocused output of a cw CO_2 laser. The probability of electron detachment is monitored as a function of irradiation period, laser intensity, wavelength and neutral gas pressure. Infrared photodetachment spectra of $C_6H_5CH_2^-$ and $C_6D_5CD_2^-$ exhibit bands at 945 and 932 cm^{-1}, respectively, while the spectrum of cyclo-$C_7H_7^-$ shows only a slight dependence on laser frequency between 920 and 1080 cm^{-1}. The photodetachment kinetics of $C_6H_5CH_2^-$ have been modeled using estimated transition rate constants between nine energy levels equally spaced by the energy of a laser photon. Comparison of the calculated results with experimental data suggests that one step in the laser excitation process is rate limiting. Radiative relaxation does not appear to be significant at laser intensities greater than 10 W cm^{-2} and collisions with neutral molecules are only moderately effective in deactivating vibrationally excited anions.

INTRODUCTION

Since the development of very high power pulsed infrared lasers, much attention has been given to understanding the processes by which isolated molecules absorb many infrared photons and subsequently dissociate or isomerize.[1-4] Although this process usually takes the form of breaking chemical bonds (multiphoton dissociation), Brauman and coworkers have reported multiphoton electron detachment (MED) of benzyl anion using a CO_2-TEA laser.[5] Such a process is especially interesting because vibrational and electronic degrees of freedom must be intimately coupled. An intriguing theoretical analysis of vibrationally driven electron detachment has recently been presented by Simons.[6]

We have explored the technique of multiphoton dissociation using a low power cw CO_2 laser[7, 8] in which vibrational excitation of positive ions trapped at low pressures takes place over a period of several hundred milliseconds. By monitoring the dissociation yield as a function of laser wavelength, infrared spectra of ions have been easily obtained in a number of cases.[9-13] In a preliminary report, we demonstrated that multiphoton electron detachment from benzyl and cycloheptatrienyl anions could be achieved using the low power laser and that the two structural isomers may be easily distinguished on the basis of their MED spectra.[14]

In this paper, we give a more detailed account of the photophysical processes associated with multiphoton electron detachment of $C_7H_7^-$ isomers using a low power cw CO_2 laser. Results are presented which characterize various aspects of multiphoton electron detachment kinetics including the dependence of the detachment yield on laser intensity and wavelength. Since the excitation occurs over a relatively long time period, the effects of collisional and radiative relaxation processes have been

probed and the results for benzyl anion have been interpreted on the basis of a model which attempts to account for the experimental observations.

EXPERIMENTAL DETAILS

The theory techniques and instrumentation of trapped ion ICR spectrometry have been previously described in detail.[15] The spectrometer used in this study was built at Caltech and incorporates a 15-in. electromagnet capable of 23.4 kG. A flat ICR cell is utilized in which one of the source plates is replaced with a 92% transmittance mesh to allow irradiation of trapped ions.

All ICR experiments were carried out in the range 10^{-7}-10^{-5} Torr, corresponding to neutral particle densities of 3×10^{9} to 3×10^{11} molecules cm^{-3}. Pressure is measured with a Schulz-Phelps type ionization gauge which is calibrated against an MKS Instruments Baratron Model M90H1-E capacitance manometer for each reagent. It is expected that absolute pressure determinations are accurate within ± 20% using this method. Methyl nitrite was prepared by a standard procedure.[16] Toluene, toluene-d_8 and cycloheptatriene were obtained commercially and used without further purification except degassing at liquid nitrogen temperature.

Figure 1 shows a schematic view of the experimental apparatus and optical configuration. The output of Apollo 550A line tunable cw CO_2 laser is directed into the vacuum chamber through a polished NaCl window. After passing through the mesh and the ion trapping region, the beam is reflected off the polished rear source plate and back out the window to a beam stop. Laser power is monitored using a Laser Precision Corp. Model RkP-345 pyroelectric radiometer and laser frequency deter-

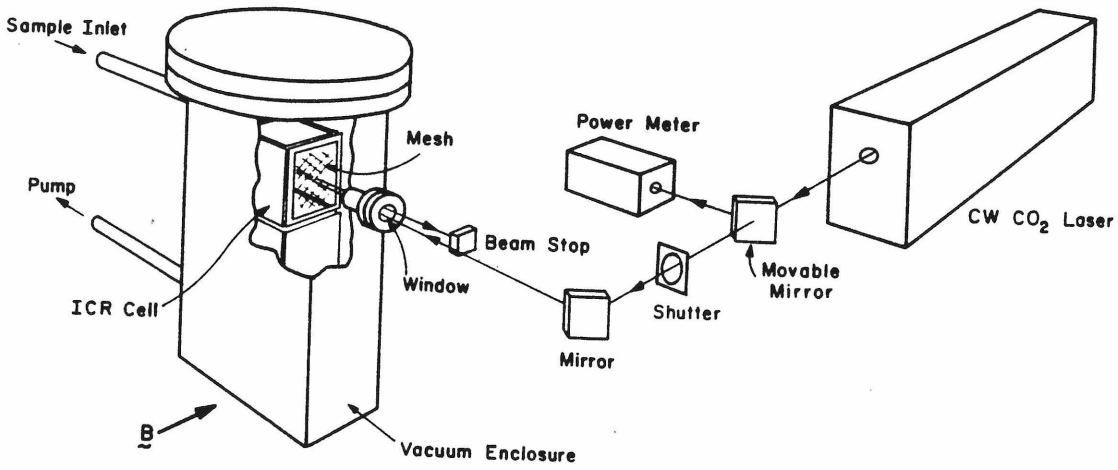

FIG. 1. Schematic view of the optical configuration. The direction of the magnetic field is indicated by $\underset{\sim}{B}$ (magnet not shown).

mined using an Optical Engineering Model 16A spectrum analyzer. Power fluctuations are typically less than ± 5% and maximum stability is achieved by running the laser continuously and controlling the irradiation with a Uniblitz Model 225LOA14X5 mechanical shutter. The shutter may be gated electronically and has a measured opening time of 5 msec. Further details of the optical configuration are given elsewhere.[17]

In a typical experiment, a 10 msec electron beam pulse initiates ion formation, followed by a trapping period up to several seconds during which reactions may occur. The ions are then mass analyzed to determine the relative concentrations of species present. Ions of a particular mass to charge ratio may be selectively ejected from the ion trap using ICR double resonance, allowing positive identification of reaction pathways.

The ions may be irradiated on alternate trapping cycles and the corresponding ion signals (laser on and laser off) monitored by a two channel boxcar integrator. These signals are then processed in a straightforward manner to yield photodetachment rate constants, even in the presence of ion loss due to diffusion and reaction.

RESULTS AND DISCUSSION

Ion Formation

Dissociative attachment of low energy electrons to methyl nitrite produces methoxide ion, CH_3O^-, which reacts with toluene and cycloheptatriene forming the $C_7H_7^-$ ions of interest.

$$CH_3O^- + C_6H_5CH_3 \rightarrow C_6H_5CH_2^- + CH_3OH \qquad (1)$$

$$CH_3O^- + \text{cyclo-}C_7H_8 \rightarrow \text{cyclo-}C_7H_7^- + CH_3OH. \qquad (2)$$

Formation of benzyl and cycloheptatrienyl anions is 0. 2 and 5. 3 kcal/mol

exothermic, respectively.[18]

Electrons which are detached from $C_7H_7^-$ isomers as a result of laser excitation remain in the ion trap. Subsequent reattachment to methyl nitrite regenerates $C_7H_7^-$ by way of Eqs. (1) and (2) eventually leading to a photostationary state. In order to simplify evaluation of the photodetachment kinetics, CH_3O^- is continuously ejected from the ion trap starting just prior to laser irradiation, thus preventing recycling of electrons during the irradiation period.

Photodetachment Kinetics

Irradiation of benzyl anion with the CO_2 laser results in electron detachment and loss of ion signal as shown in Fig. 2. The exponential (first order) decay is what might be expected for a single photon process except for a slight induction period which precedes the onset of the decay. As the laser intensity is lowered to about 10 W cm^{-2}, the induction period becomes much longer as shown in Fig. 3.

The dependence of the photodetachment rate constant on laser intensity may be found by plotting ln (I_0/I) versus intensity (Fig. 4), where I and I_0 are the ion signals in the presence and absence of laser irradiation. For intensities greater than about 10 W cm^{-2}, this function is found to be linear. However at low intensities, the induction period becomes large compared with the irradiation period and no loss of benzyl anion is observed. The photodetachment kinetics are similar for cycloheptatrienyl anion except that the observed induction periods are much smaller and appreciable electron detachment is observed at lower laser intensities.

Since multiphoton electron detachment occurs over a period of several hundred milliseconds under these conditions, collisional

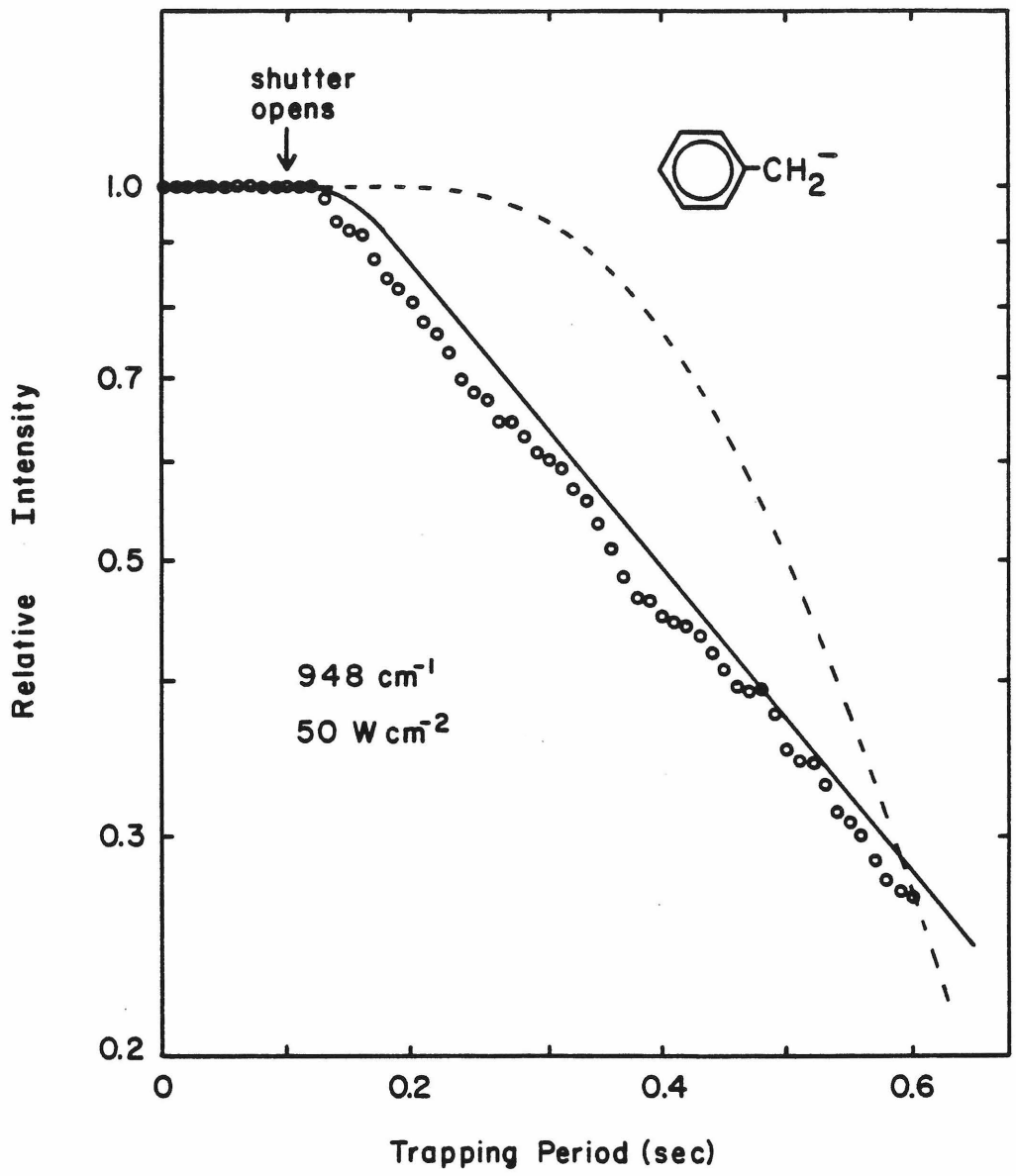

FIG. 2. Semilogarithmic plot of I/I_0 vs. trapping period for benzyl anion, where I and I_0 are the ion signals in the presence and absence of laser irradiation, respectively. The mechanical shutter opens at 100 ms. Laser intensity is 50 W cm^{-2} at 948 cm^{-1}. Neutral pressures of methyl nitrite and toluene are 2×10^{-8} and 4×10^{-7} Torr, respectively. The open circles represent experimental data while the solid and dashed curves are calculated using the kinetic model outlined in the text.

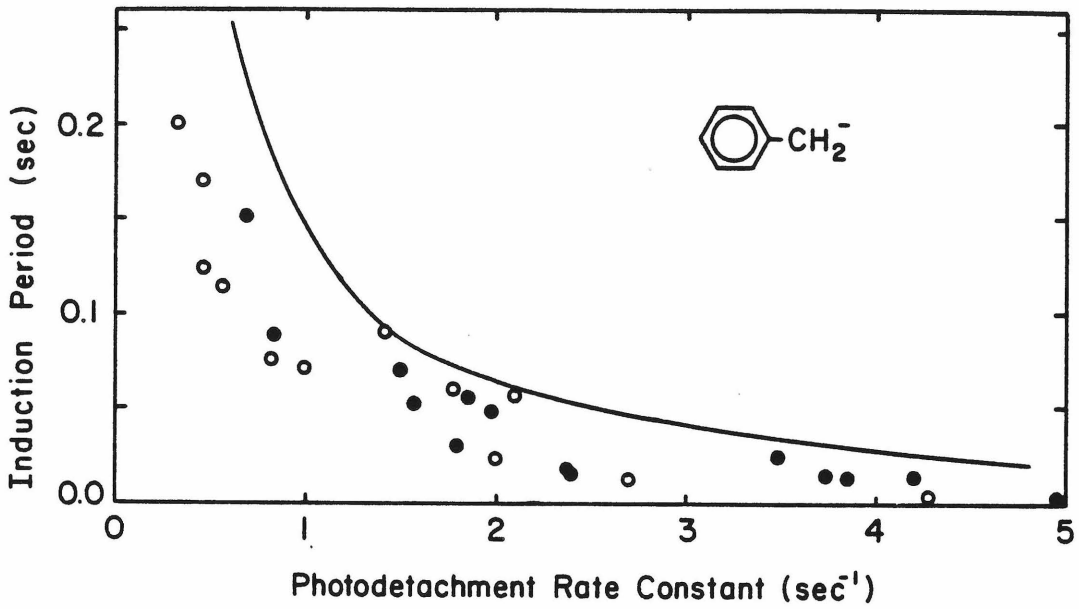

FIG. 3. Variation of the induction period with photodetachment rate constant. The two sets of data (open circles and solid points) were obtained in separate experiments in which the apparent photodetachment cross sections were slightly different due to different overlaps of the laser beam and ion cloud in the ICR spectrometer. The curve is calculated using the kinetic model discussed in the text.

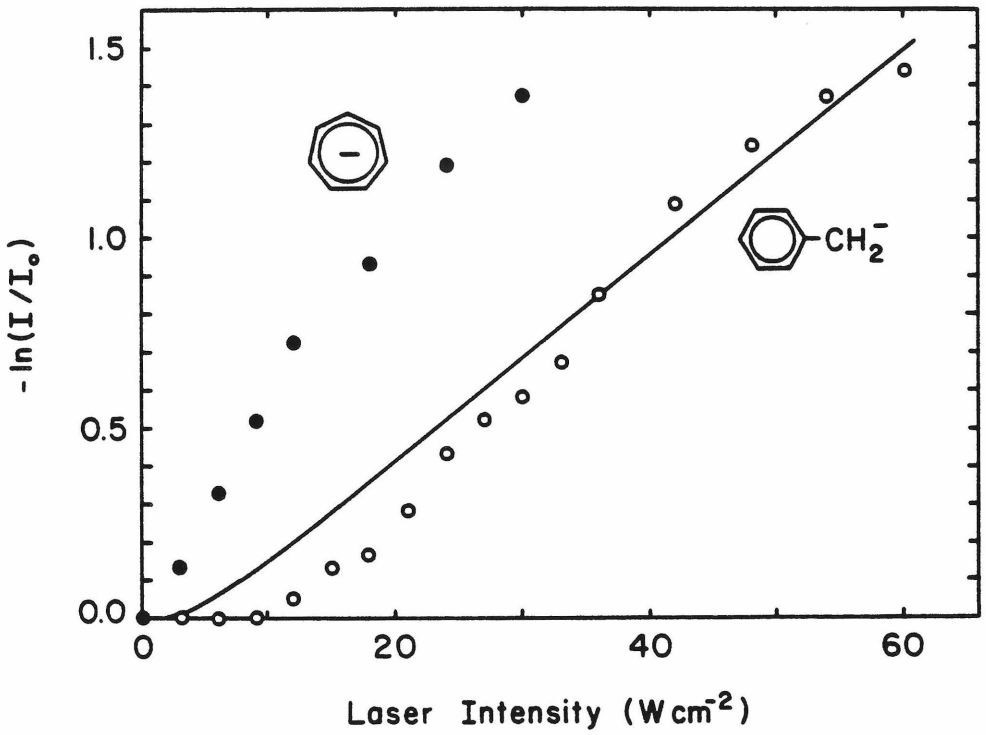

FIG. 4. Variation of $-\ln(I/I_0)$ with laser intensity for cycloheptatrienyl anion (solid points) and benzyl anion (open circles). Irradiation was for 500 ms at 948 cm^{-1}. The solid curve is calculated for benzyl anion using the kinetic model discussed in the text.

relaxation may be important in determining the overall photodetachment rate due to deactivation of vibrationally excited intermediates. The variation of photodetachment yield vs. pressure is shown in Fig. 5 for cycloheptatrienyl and benzyl anions. Interestingly, there is a significant range of pressures below 2×10^{-6} Torr in which collisions have no apparent effect on the photodetachment yield. The drop in yield in the 10^{-6} Torr pressure range may be ascribed to vibrational deactivation as a result of collisions with C_7H_8 neutrals. Symmetric proton transfer would be an effective process for energy relaxation[19] in these systems; however, the rate constants for benzyl anion[20] ($k = 3 \times 10^{-12}$ cm^3 molecule^{-1} sec^{-1}) and several other delocalized anions are quite small. With the exception of these data, all of the experimental results presented in this paper pertain to the low pressure region at approximately 4×10^{-7} Torr.

Spontaneous emission of infrared radiation also has a potentially significant role in the deactivation of excited molecules containing insufficient energy for electron detachment. Just as collisional deactivation is probed by allowing greater numbers of collisions during the irradiation period, the effects of radiative emission may be probed by increasing the irradiation period while decreasing the laser intensity to keep the total fluence (J cm^{-2}) constant. The data in Fig. 6 show that the photodetachment yield is found to be constant, within experimental uncertainty. Thus radiative emission is found to be relatively unimportant in the overall photodetachment kinetics except possibly at very low laser intensities (< 10 W cm^{-2}) where experimental uncertainty is greatest.

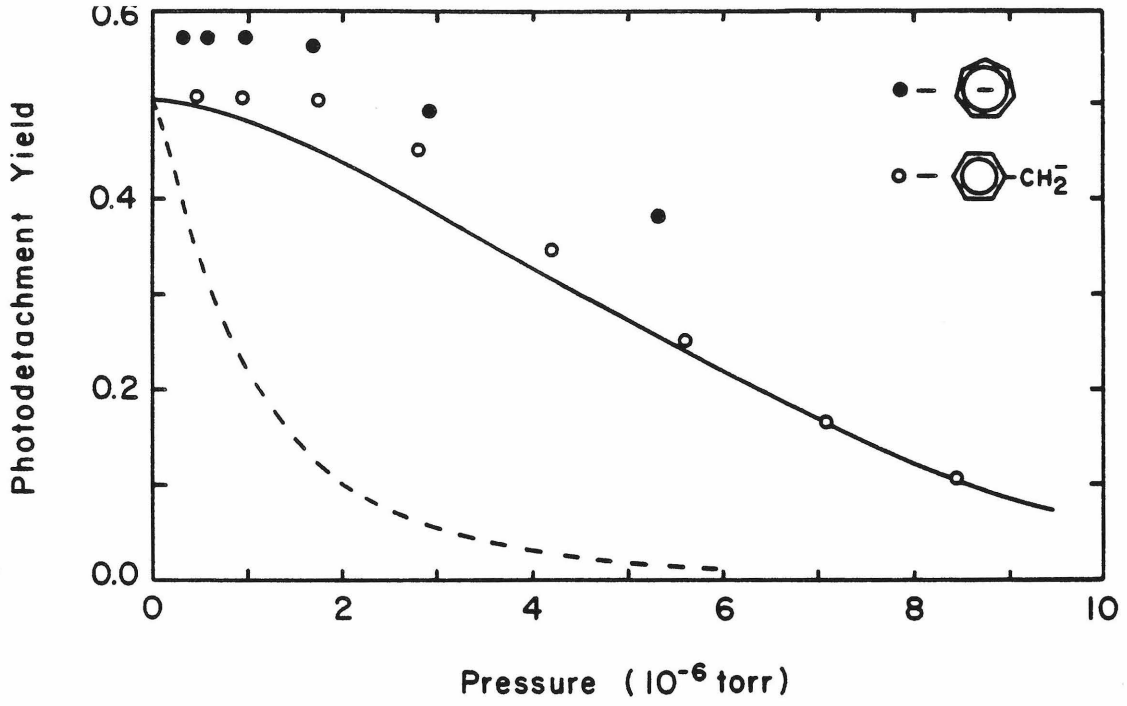

FIG. 5. Pressure dependence of the multiphoton electron detachment yield for cycloheptatrienyl anion (solid points) and benzyl anion (open circles). For all data the pressure of methyl nitrite is 1.0×10^{-7} Torr with neutral C_7H_8 making up the balance. Results of a model calculation for benzyl anion are shown for strong collisions removing all of the internal energy of the anion (dashed curve) and weaker collisions which remove only 25% of the internal energy (solid curve).

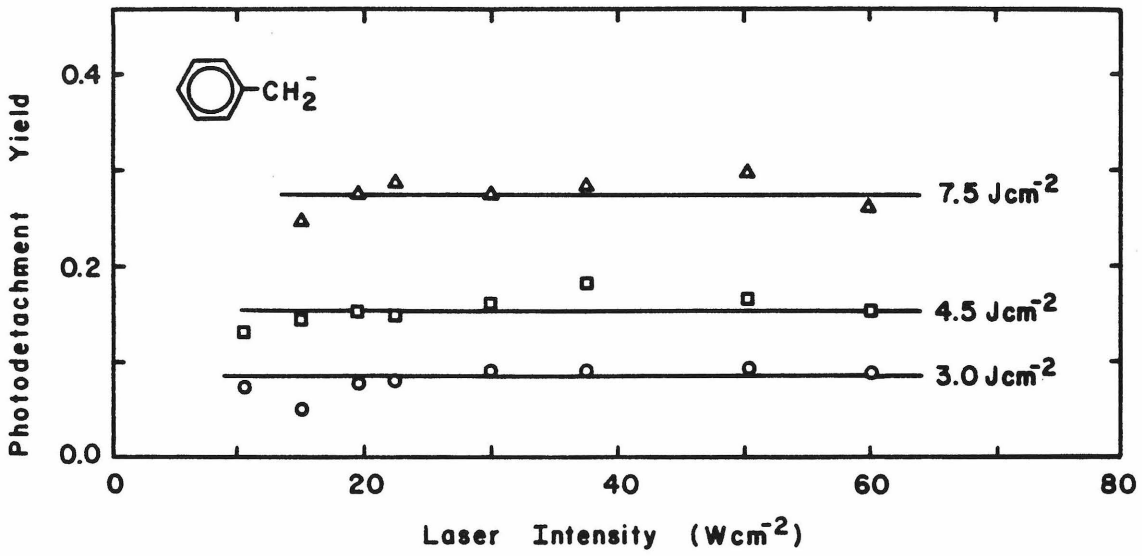

FIG. 6. Plot of multiphoton electron detachment yield vs. laser intensity at constant fluence. Yield is constant within experimental uncertainty for three different fluence levels.

Photodetachment Spectra

Infrared multiphoton electron detachment spectra for benzyl and cycloheptatrienyl anions are obtained by monitoring the photodetachment yield as a function of laser frequency at constant intensity and irradiation period, Fig. 7a. While the yield for cyclo-$C_7H_7^-$ is nearly independent of frequency over the tuning range of the CO_2 laser, benzyl anion presents a characteristic band with a maximum at 945 cm^{-1}. The technique thus displays a remarkable isomeric selectivity at frequencies above 1000 cm^{-1}. As was pointed out in a previous paper,[14] multiphoton electron detachment is well suited to identification of isomeric structures in mass spectrometry and can also be used to quantitatively determine the composition of a mixture of isomers.

One interesting feature of the spectra is that although the frequency bandwidth of the laser (estimated to be 1.7×10^{-3} cm^{-1}) is much narrower than the spectral features observed (≥ 30 cm^{-1}), photodetachment of all the molecules occurs at a single wavelength. Either all of the molecules absorb at all wavelengths within the spectral band simultaneously (homogeneous broadening) or vibrational and rotational state redistribution is fast on the time scale of the irradiation period, allowing each molecule to "sample" the laser bandwidth many times during irradiation. Comparison of the TEA laser spectrum[21] with the cw laser results in Fig. 7 suggests that the bands are indeed homogeneously broadened since the TEA laser pulse lasts only 10^{-6} sec making the detachment process truly collision free. The photodetachment cross section for TEA laser excitation is about four times that for cw irradiation. Photodetachment also occurs over a wider range of frequencies using the TEA laser although the reasons for this are not clear. Pulsed CO_2-TEA

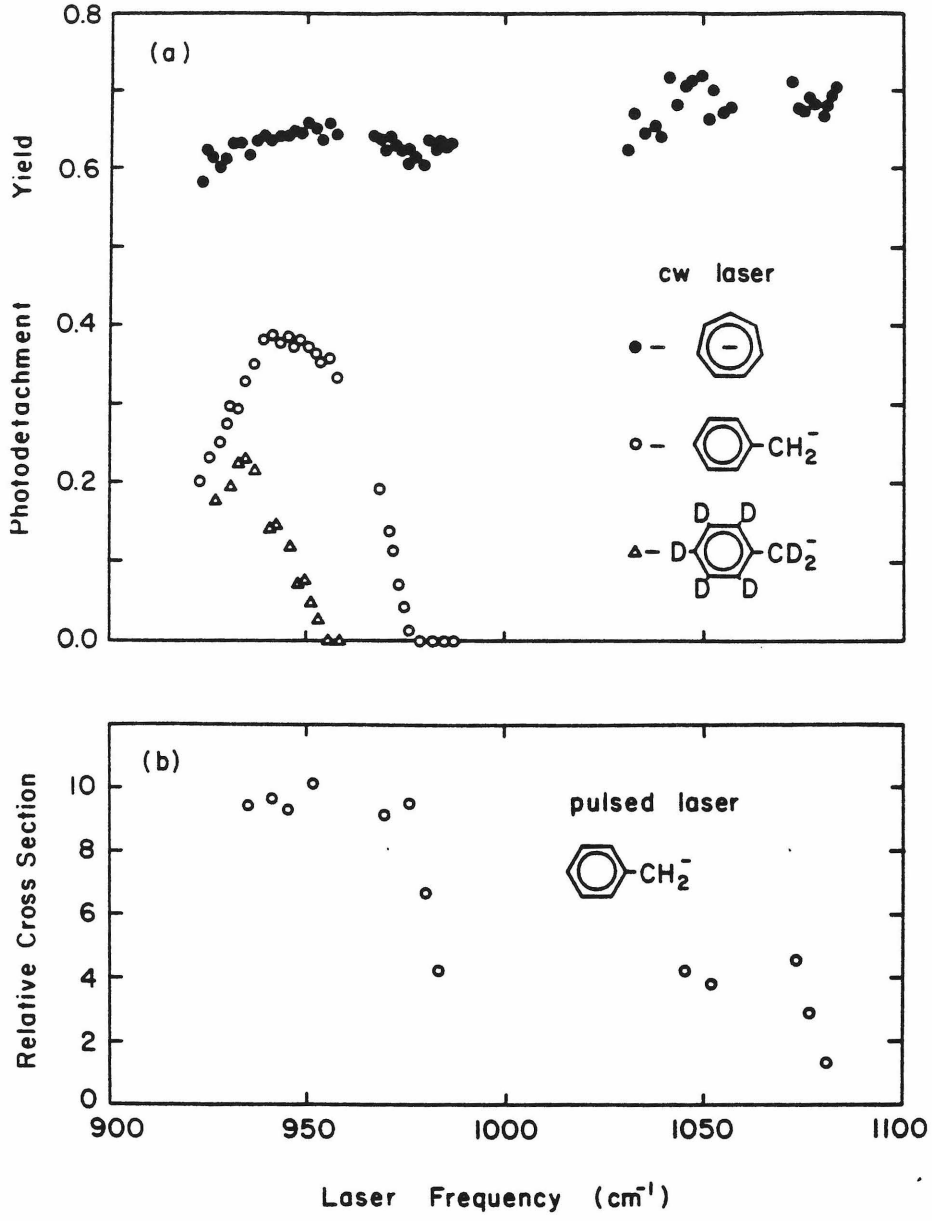

FIG. 7. Multiphoton electron detachment spectra of $C_7H_7^-$ anions. (a) Continuous wave laser yields for cyclo-$C_7H_7^-$, $C_6H_5CH_2^-$ and $C_6D_5CD_2^-$ for a 500 ms irradiation period at 24 W cm^{-2}. Yields for benzyl and benzyl-d_7 anions are zero above 1000 cm^{-1}. (b) Pulsed TEA laser spectrum of benzyl anion from ref. 21 showing relative cross section vs. frequency. The (phenomenologically defined) detachment cross section at 935 cm^{-1} is approximately four times that using the cw laser at the same frequency.

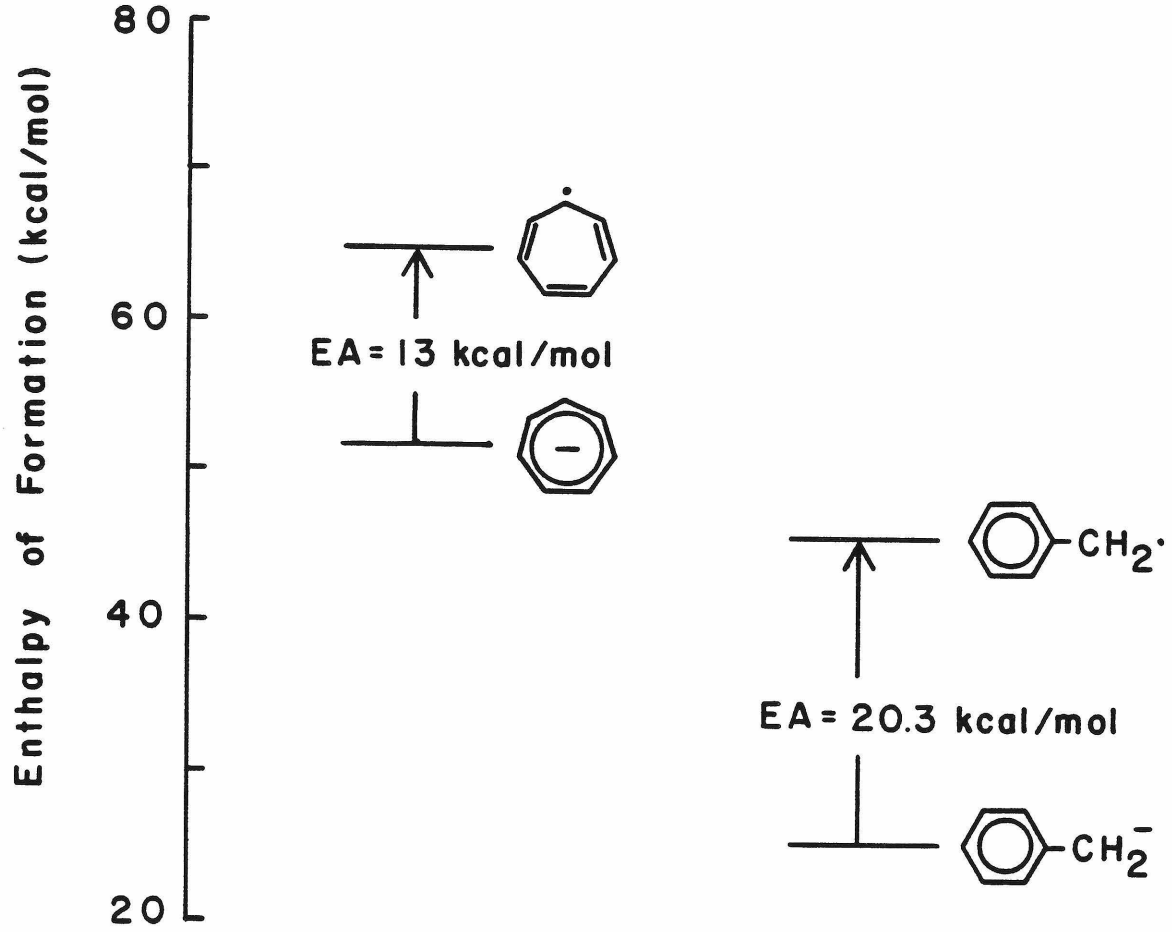

FIG. 8. Diagram showing the ground state energies of C_7H_7 radicals and anions. Isomerization of cycloheptatrienyl anion to a six-membered ring should result in autodetachment of an electron to form benzyl radical.

laser and cw laser photodissociation spectra[10] of CF_3I^+ were found to be identical. Comparison of results in other photochemical systems will probably be required before the differences between pulsed and continuous excitation may be properly assessed.

In addition to isomeric selectivity, multiphoton electron detachment exhibits isotopic selectivity as shown in Fig. 7a. The MED spectrum of $C_6D_5CD_2^-$ overlaps that of $C_6H_5CH_2^-$, but the band is narrower and its maximum lies 12 cm^{-1} to lower energy. The lower photodetachment yields are due primarily to a much longer induction period compared with $C_6H_5CH_2^-$. Examination of the vibrational mode assignments for toluene[22] reveals that transitions in the 920-1080 cm^{-1} region shift an average of 128 cm^{-1} to lower energy upon deuteration to $C_6D_5CD_3$. For this reason it is unlikely that the bands observed for $C_6H_5CH_2^-$ and $C_6D_5CD_2^-$ correspond to the same molecular vibration.

Kinetic Model of Multiphoton Electron Detachment

One of the objectives in studying infrared laser-induced chemical reactions is to better understand the mechanism by which many photons are sequentially absorbed by a molecule. Individual absorption and deactivation events are difficult to probe directly, however, and usually the only physical observable is the overall decay (or production) of a population of molecules. With this limitation in mind it is often instructive to construct simple models which can provide some qualitative insight to the excitation mechanism by reproducing various characteristics of the observed photochemical kinetics.

Benzyl anion was chosen as the system to model for several reasons. First, although the vibrational frequencies of the anion are unknown, they are easily estimated using toluene as a model compound.

The electron binding energy (electron affinity of benzyl radical) is known[23] to be 20 kcal/mol whereas only an estimate of 13 kcal/mol is available for cycloheptatrienyl anion.[18] Furthermore, cycloheptatrienyl anion has at least one low lying electronic state in the region of interest,[24] complicating matters somewhat. Finally, electron detachment from cycloheptatrienyl anion might not occur as a direct process. The heat of formation[25] of cyclo-$C_7H_7^-$ is greater than that of benzyl radical plus a free electron (Fig. 8), so structural rearrangement to a six membered ring at any point during the excitation process would be expected to result in autodetachment of an electron.

In order to construct a workable model of multiphoton electron detachment, several simplifying assumptions must be made. There are approximately 4×10^7 vibrational states[26] of benzyl anion with energy less than 20 kcal/mol, the adiabatic electron affinity of benzyl radical. Since a minimum of eight infrared photons must be absorbed to reach this level of internal excitation, we will consider a model with nine energy levels each spaced by the energy of one laser photon. Transitions between these levels may be induced by photon absorption, radiative emission and collisional deactivation. Once the highest energy level is reached it is assumed that the electron detachment rate is fast compared with other transition rates.

Simons[6] has correctly pointed out that the threshold for vibrationally driven electron detachment may occur at substantially higher energy than the adiabatic electron affinity if the electronic potential surfaces of the anion and radical do not cross. Consideration of the torsion angle potential of the CH_2 group in benzyl anion provides a good example of this point. The electron affinities of non-delocalized

radicals are typically zero or very small, so rotation of the methylene group such that the lone pair is orthogonal to the ring orbitals leads to a configuration which should have a very small electron binding energy and vibrationally induced electron detachment should be efficient. At lower energies, the anion and radical potential surfaces are farther apart and although the internal energy of the anion is greater than the adiabatic electron binding energy, it is metastable with respect to detachment. The danger in such simple considerations lies in the fact that true potential surfaces for such large molecules are multidimensional and crossings may occur at other points. Furthermore, the time scale of the present experiment is such that even unfavorable transitions between potential surfaces may occur at energies near the adiabatic threshold.

Continuing with the development of the kinetic model, a set of nine coupled differential equations may be written to describe all possible transition rates into and out of the various energy levels. While a complete analytical solution to the energy grained master equation is virtually unthinkable for a problem of this complexity, numerical solutions may be easily handled by a small computer or hand calculator. The approach taken in this study is an exact stochastic treatment as outlined by Barker[27] in which molecules undergo a series of trajectories or random walks between the various energy levels. Each trajectory is completed when detachment occurs or when a set time limit is exceeded. The transition probabilities are governed by predetermined rate constants and the results may be made arbitrarily precise merely by increasing the number of trajectories.

Each trajectory is begun from the lowest energy level since the

average thermal internal energy of benzyl anion at 300 K is only 1.6 kcal/mol. This value is calculated using the vibrational frequencies of toluene and assumes that no excess energy is acquired as a result of ion formation. The internal energy of cycloheptatrienyl anion is probably somewhat higher due to the exothermicity of Eq. (2).

The simplest choice for determining transition rate constants for up-pumping between adjacent energy levels is to make them all the same. Doing so, however, results in calculated population decay curves which are conspicuously non-exponential (Fig. 2) and which have induction periods which are much longer than observed for a given decay rate. The experimentally observed first order decays and the linear dependence of the photodetachment rate constant on laser intensity suggest that one of the absorption steps is severely rate limiting. The "bottleneck" is presumably one of the first steps in the absorption process although there is no direct evidence for this. Setting the cross section for absorption of the first photon equal to 1.0×10^{-21} cm^2 and the remainder of the absorption cross sections to 50.0×10^{-21} cm^2 gives good agreement between the calculated and experimental decay curves in Fig. 2.

Radiative emission rates between the various energy levels are somewhat more difficult to obtain; however, crude estimates for benzyl anion are obtained using the basic method outlined by Dunbar.[28] Using toluene as a model compound, spontaneous emission rate coefficients are calculated for infrared active vibrational modes using integrated infrared absorption spectra (Table I). Assuming a thermal distribution of internal energy over the various vibrational modes, transition rate constants between the energy levels may be estimated. The procedure

Table I. Einstein A Coefficients for Spontaneous Emission from Infrared Active Vibrations of Toluene[a]

Band Position (cm^{-1})	A (sec^{-1})
3050	58.43
2900	29.49
1610	1.97
1500	4.12
1080	0.59
1030	0.55
730	1.99
700	0.86

[a]Obtained from the gas phase infrared spectrum of toluene as outlined in the Appendix.

is outlined in the Appendix and the values listed in Table II. The calculated spontaneous emission rates are small compared with the excitation rates at moderate laser intensities. This is in good qualitative agreement with the observation that photodetachment yields for benzyl anion are independent of laser intensity at constant fluence.

Although the absorption cross sections have been chosen empirically and the radiative emission rate constants calculated from infrared spectra of toluene, a check for self-consistency is possible at this point. The rate coefficient for spontaneous emission (Einstein A coefficient) is related to the absorption cross section σ by

$$A_{10} = \frac{8\pi h\nu^3}{c^2} B_{10} \frac{\Delta\nu_{trans}}{\Delta\nu_{laser}} = \frac{8\pi\nu^2\sigma\Delta\nu_{trans}}{c^2} \qquad (3)$$

where $\Delta\nu_{laser}$ and $\Delta\nu_{trans}$ are the bandwidths of the laser and molecular transition, respectively. The laser stimulated emission rate coefficient B_{10} is equal to that for absorption when non-degenerate vibrations are considered. Using the empirical absorption cross section $\sigma = 50.0 \times 10^{-21}$ cm^2 and a transition bandwidth of 35 cm^{-1} from Fig. 7, Eq. (3) gives $A_{10} = 1.2$ sec^{-1}, in good agreement with the values calculated for toluene listed in Table I.

Using the empirically derived absorption cross sections and the spontaneous emission rate constants in Table II, the model reproduces many of the observed features of the photodetachment kinetics. Calculated curves of photodetachment yield vs. irradiation period show that the decay of ion population with irradiation period is exponential (Fig. 2). The induction periods calculated using the model display the correct qualitative intensity dependence but the values are larger than observed

Table II. Spontaneous Emission Rate Constants[a] Used for Model Calculations[b]

Initial Internal Energy	Final Internal Energy (kcal/mol)						
	0	2.71	5.42	8.13	10.83	13.54	16.25
2.71	0.15	0.03	0.00	0.01			
5.42		0.29	0.07	0.06	0.02		
8.13			0.46	0.12	0.13	0.04	
10.83				0.63	0.17	0.22	0.06
13.54					0.80	0.22	0.33
16.25						0.98	0.27
18.96							1.14

[a]Rate constants have units of sec^{-1}.

[b]Calculated from infrared spectra of toluene and adjusted for a model having equally spaced energy levels.

experimentally.

There are many different ways to account for collisional deactivation using the model. The dashed curve in Fig. 5 illustrates the effect of "strong collisions" which remove all of the internal energy in the anion. Such a description might be appropriate to describe reactive collisions in which transfer of a proton from a cold toluene molecule to a hot benzyl anion would leave the resultant anion with very little internal energy. The disagreement with experiment is apparent. The solid curve, calculated for weak collisions which remove only 25% of the internal energy, gives better overall agreement with experiment, but predicts too sharp a drop in yield at low pressures. One possible explanation for absence of a pressure dependence in the experimental points below 2×10^{-6} Torr is that collisions may enhance the overall photodissociation rate by increasing the transition rates at one or more steps. A similar effect has been reported as collision enhanced multiphoton dissociation[9] of $C_3F_6^+$. At low pressures the deactivation and enhancement effects may accidentally cancel, giving the misleading impression that collisions have no effect at all on the transition rates between energy levels.

At this point it is worthwhile to assess the validity of the model in determining the microscopic transition rates between the various energy levels. Obviously the available data do not permit a unique determination of each rate constant incorporated into the model. This type of approach may be instructive, however, for gaining a qualitative understanding of the relative importance of various rate constants in determining the overall photodetachment kinetics. Radiative emission, for instance, is believed to play a relatively unimportant role.

Collisions are only moderately effective at deactivating excited intermediates and there is some suggestion that they may enhance the net excitation rate at one or more steps. Finally, the shape of the decay curves strongly suggests that the net rate of photon absorption at one step is much slower than the rest.

Many questions relating to the photophysics of multiphoton excitation remain unanswered. What is the nature of the bottleneck in the absorption steps? Why is the apparent multiphoton electron detachment cross section larger for the pulsed laser experiments than for continuous irradiation? Why are the calculated induction periods much larger than observed? Some insight may be drawn by considering the density of vibrational states of benzyl anion (Fig. 9). At internal energies less than about 8 kcal/mol, vibrational states are relatively sparse so that once a photon is absorbed, transfer of the energy from the pumped vibrational mode to the remaining modes (the molecular heat bath) may not be very efficient. If the energy remains in the pumped mode long enough, energy removal by stimulated emission may become important. Use of pulsed laser offers the possibility that coherent excitation and/or power broadening helps to overcome this bottleneck by inducing a closer coupling between the pumped mode and the intramolecular heat bath. If a sparse density of states is the source of the bottleneck, then the extent to which a particular molecule is affected depends on its initial energy before laser irradiation begins. The average value of this initial energy is 1.6 kcal/mol; however, molecules with greater energies would be expected to dissociate faster than those with less. Some reduction in the induction periods would be expected from those calculated using the model considered here. Obviously a much more complex model is

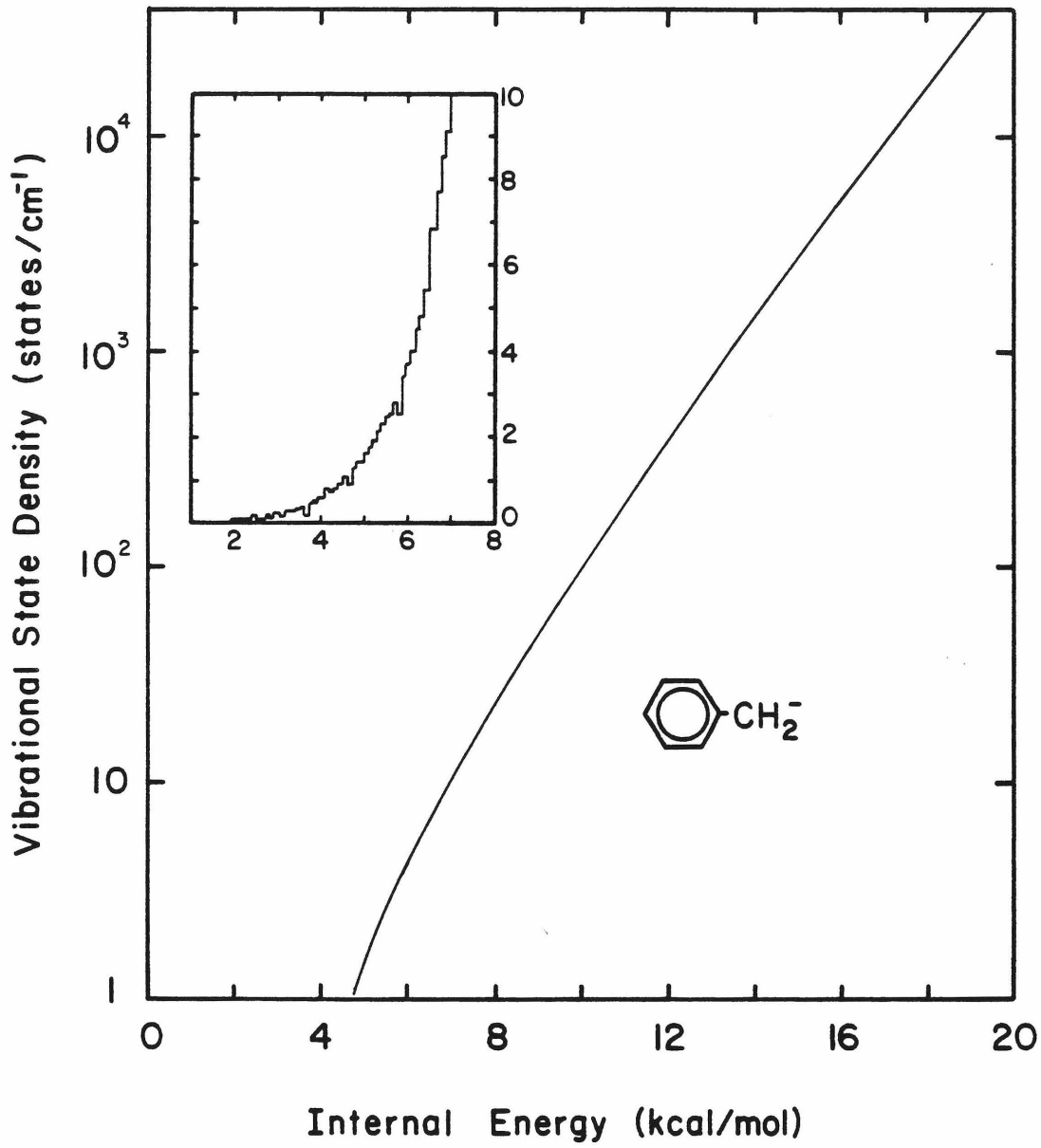

FIG. 9. Vibrational state density of benzyl anion as a function of internal energy. Thirty-six vibrational frequencies of toluene were used in the calculation. The Whitten-Rabinovitch approximation was used for $E > 7$ kcal/mol while the low energy points are the result of a direct count. Note that the large plot is semilogarithmic while the inset at low energies is linear.

required in order to treat multiphoton excitation of molecules with a distribution of initial internal energies.

While such considerations are speculative at this point, it is hoped that continued studies of multiphoton dissociation and multiphoton electron detachment will provide an opportunity to further refine the mechanism of vibrationally driven unimolecular reactions.

CONCLUSIONS

Multiphoton electron detachment provides a convenient method for obtaining infrared spectra of molecular anions. The ability to distinguish structural isomers in this way is of considerable interest since a general method would greatly extend the capabilities of mass spectrometry. While the wavelength regions currently accessible are limited, development of intense widely tunable infrared lasers will give experimentalists access to more complete spectra. High resolution spectra and vibrational assignments will help to gain a better understanding of molecular structure and bonding in anions.

Many of the features which characterize the kinetics of multiphoton electron detachment are similar to those observed for multiphoton dissociation of positive ions. In both cases, unimolecular detachment or dissociation is presumed to be fast compared with deactivation or laser excitation when low power cw lasers are used. Thus, while little information concerning detailed coupling of vibrational and electronic degrees of freedom can be gained from these experiments, some aspects of multiphoton excitation processes may be probed. Comparison of the available data with results predicted by models affords a qualitative understanding of the relative importance of collisional and radiative relaxation processes and photon absorption rates in determining the overall kinetic

behavior of multiphoton electron detachment.

ACKNOWLEDGEMENTS

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APPENDIX

In this section, we describe how spontaneous emission rate constants for benzyl anion were calculated as a function of internal energy. To begin, we note the well known relation between the Einstein A and B coefficients for spontaneous emission and stimulated absorption of radiation,

$$A_{10} = \frac{8\pi h \nu^3}{c^2}\left(\frac{g_1}{g_0}\right) B_{01} \qquad \text{(A1)}$$

Here, g_1 and g_0 represent the degeneracies of the upper and lower states and B_{01} is expressed in so-called "intensity units" of $cm^2 erg^{-1} s^{-1}$. Furthermore, we can calculate the value of B_{01} for any absorption band by integrating the absorption cross section over the band,

$$B_{01} = \int \frac{\sigma_\nu \, d\nu}{h\nu} \approx \frac{1}{h\nu_0} \int \sigma_\nu \, d\nu . \qquad \text{(A2)}$$

For stable neutral molecules, the cross section σ_ν in units of cm^2 is conveniently obtained from an ordinary infrared absorption spectrum by the relation

$$\sigma_\nu = \frac{-\ln(I/I_0)}{N\ell} \qquad \text{(A3)}$$

where I/I_0 is the percent transmission, ℓ is the sample path length and N is the sample concentration in molecules cm^{-3}. Combining Eqs. (A1) - (A3) gives

$$A_{10} = \frac{8\pi \nu_0^2 g_1}{c^2 N \ell g_0} \int -\ln(I/I_0) d\nu \qquad \text{(A4)}$$

The Einstein coefficients for several infrared bands of toluene are given

in Table I.

We will now make the rather crude approximation that the internal degrees of freedom in the molecule may be treated as a collection of uncoupled harmonic oscillators, except that energy is freely exchanged between the various modes. Spontaneous emission may occur only between adjacent levels of each oscillator ($\Delta v > 1$ processes are ignored) and the various rate coefficients are given by

$$A_{n,\,n-1} = n A_{10} \tag{A5}$$

The total emission rate constant for one oscillator is the sum of the rate coefficients for each level of the oscillator weighted by the probability that the level is occupied.

$$k^{i}_{rad}(E) = \sum_{n} P^{i}_{n}(E) n A^{i}_{10} \tag{A6}$$

$$P^{i}_{n}(E) = \frac{\exp(-nh\nu_i/kT)}{\sum_{n}\exp(-nh\nu_i/kT)} \tag{A7}$$

A Boltzmann distribution among the levels is assumed and the characteristic temperature T depends on the total internal energy of the molecule, E. The explicit temperature dependence of E may be calculated by summing the average energy of each vibrational mode over the total number of modes,

$$E = \sum_{i} h\nu_i \left[\exp(h\nu_i/kT)-1\right]^{-1} \tag{A8}$$

or by using tabulated values[29] of enthalpy $H-H_0$ versus temperature. The internal energy E is related to enthalpy by

$$E = H - H_0 - 4RT \tag{A9}$$

The values in Table II were calculated using the latter method.

The denominator in Eq. (A7) is the vibrational partition function for mode i

$$q_i = \sum_n \exp(-nh\nu_i/kT) = [1-\exp(-h\nu_i/kT)]^{-1}. \tag{A10}$$

Combining Eqs. (A6), (A7) and (A10) gives

$$k^i_{rad} = [1-\exp(-h\nu_i/kT)]A^i_{10} \sum_n n\exp(-nh\nu_i/kT) \tag{A11}$$

We note that for $x^2 < 1$

$$\sum_n nx^n = \frac{x}{(1-x)^2} \tag{A12}$$

So for $x = \exp(-h\nu_i/kT)$, Eq. (A11) becomes

$$k^i_{rad} = A^i_{10}[\exp(h\nu_i/kT)-1]^{-1} \tag{A13}$$

For each infrared mode, i, we can now calculate the rate constant for radiative emission at frequency ν_i as a function of internal energy. In general, however, the energy of the emitted photon does not equal the spacing between the nine levels in the model. For instance, emission at 1500 cm^{-1} decreases the internal energy by more than one 945 cm^{-1} step, but less than two. The rate constant, k_{rad} is then apportioned between k_{-1} and k_{-2} such that the total emission rate and the total energy emitted remains constant:

$$k_{rad} = k_{-1} + k_{-2} \tag{A14}$$

$$k_{rad}(1500) = k_{-1}(945) + k_{-2}(1890) \tag{A15}$$

Solution of these two equations gives

$$k_{-1} = k_{rad} \frac{(1890-1500)}{(1890-945)} = 0.413\ k_{rad} \tag{A16}$$

$$k_{-2} = k_{rad} - k_1 = 0.587\ k_{rad} \tag{A17}$$

Similar treatment for the other frequencies in Table I results in the transition rate constants given in Table II.

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CHAPTER IV

Infrared Spectra of Butenyl Anions. Multiphoton Electron Detachment as a Photochemical Probe of Isomeric Structures of Gas Phase Anions.

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Abstract

The techniques of ion cyclotron resonance spectroscopy have been used to examine infrared multiphoton electron detachment reactions of $C_4H_7^-$ structural isomers. Anions are trapped at low pressure for up to several seconds during irradiation with the unfocused output of a line tunable continuous wave CO_2 laser. By examining photodetachment yields as a function of laser wavelength and irradiation period it is possible to distinguish three different structural isomers. Deprotonation of cis-2-butene by NH_2^- and H^- forms exclusively cis-1-methylallyl anion whereas deprotonation of trans-2-butene or 1-butene yields a mixture of the cis and trans anions. The third isomer, 2-methylallyl anion, results from deprotonation of 2-methylpropene. Infrared multiphoton electron detachment spectra in the 10 micron region are presented for these anions and isomeric mixtures.

INTRODUCTION

Several mass spectrometric techniques have recently been developed to probe the molecular structures of ions. Collision induced dissociation of mass selected ions[1, 2] has been used to analyze the compositions of complex chemical mixtures. While this technique is well suited to identification of functional groups in large molecules, fragmentation patterns of isomeric ions are often similar,[3] making these distinctions difficult. Ions having the same mass to charge ratio but radically different structures may usually be distinguished on the basis of reactivity toward specific neutral reagents. Propargyl anion ($HC \equiv CCH_2^-$), for example, reacts with O_2 at a rate seven times faster than its geometric isomer, methylacetylide anion ($CH_3C \equiv C^-$).[4] Other isomeric ions are commonly identified on the basis of their acid-base properties.[5] As isomers become functionally and geometrically more similar, though, differences in their reactive properties become harder to discern.

One example of considerable recent interest has been attempts to determine the relative thermodynamic stabilities of cis and trans-butenyl anions. In complexes with positively charged metal centers, butenyl anions are known to adopt a surprising preference for the cis configuration. By evaluating the equilibrium isomeric compositions of these complexes under a variety of conditions, Schlosser and Hartmann were able to conclude that this preference is due to the greater stability of the free cis anion rather than to effects of metal binding or solvation.[6]

It had been noted much earlier[7] that base catalyzed isomerization

of 1-butene produces more cis-2-butene than trans-2-butene despite the fact that the latter lies lower in energy by 1.1 kcal/mol.[8] This kinetic preference is believed to be due in part to the greater stability of the cis anion compared with the trans.[9] Ab initio[10] and semi-empirical[11] calculations have also found the cis anion to be slightly more stable than the trans.

Bartmess and coworkers attempted to determine the gas phase acidities of 2-butenes by equilibrium proton transfer measurements with OH^- and $C_3H_5^-$, and concluded that the trans-butenyl anion is more stable than its cis isomer by 0.2 kcal/mol.[12] The validity of this measurement was cast in some doubt by DePuy et al.,[4,13] who suggested that multiple proton transfer events during a single collision of OH^- with either 2-butene isomer could lead to a mixture of cis and trans anions. These workers attempted to form pure butenyl isomers by base induced displacement from cis- and trans-1-(trimethylsilyl)-2-butene, but were unable to distinguish any differences in reactivity of the anions formed.[4]

We have recently demonstrated that multiphoton dissociation and multiphoton electron detachment are sensitive probes of ionic structures for distinguishing between isomers. Using low power cw CO_2 laser excitation, an infrared spectrum of an ion is obtained by monitoring the extent of dissociation or electron detachment as a function of laser wavelength at a fixed laser intensity and irradiation period. It was demonstrated that electron impact ionization of perfluorocyclopropane is accompanied by quantitative ring opening to form the parent ion of perfluoropropene since the same infrared spectrum was obtained of ions from both neutral C_3F_6 isomers.[14] In another case, we showed

that proton abstraction from norbornadiene by CH_3O^- is accompanied by structural rearrangement of the hydrocarbon to give a mixture of benzyl and cycloheptatrienyl anions by comparing the spectrum of the product mixture to those of the pure $C_7H_7^-$ isomers.[15]

In this paper we describe how multiphoton electron detachment is used to distinguish cis- and trans-butenyl anions formed by proton transfer reactions in an ion cyclotron resonance spectrometer. Spectral and kinetic analysis of the electron detachment results are used to show that the cis isomer is the kinetically favored and most likely the thermodynamically more stable product of proton abstraction from both 2-butene isomers and from 1-butene. Multiphoton electron detachment spectra of cis-butenyl anion, cis-trans mixtures and 2-methylallyl anion are presented.

EXPERIMENTAL SECTION

The theory, techniques and instrumentation of trapped ion ICR spectroscopy have been described in detail elsewhere.[16,17] The cell has been modified for photochemical studies by replacing one of the plates in the ion trapping region with a 92% transmittance wire mesh. The unfocused output of a line tunable cw CO_2 laser (Apollo Model 550A) enters the vacuum enclosure through a polished NaCl window, passes through the mesh and reflects off the rear plate and back out the window in a double pass through the ion trap. The laser power is measured with a pyroelectric radiometer (Laser Precision Model RkP-345) and beam shape is monitored using a thermal imaging plate (Optical Engineering Model 22A). Irradiation of the ions is limited to alternate trapping cycles with an electronically gated mechanical

shutter (Uniblitz Model 225LOA14X5). The corresponding ion signal intensities (laser on and laser off) are monitored with a two channel boxcar integrator. Straightforward processing of the integrator outputs yields photodetachment yields even in the presence of ion loss due to diffusion and reaction. Further details are given elsewhere.[18]

Ammonia, cis- and trans-2-butene, 1-butene and 2-methylpropene were obtained commercially and used without further purification except for degassing at liquid nitrogen temperature. The isomeric purity of the butenes was verified to be $> 99\%$ by vapor phase chromatography. Separation was on a 20 ft $\times \frac{1}{8}$ in. column (15% $\beta\beta'$-oxydipropionitrile on 100/120 Chromosorb P-NAW) at 0°C.

Infrared spectra of cis- and trans-2-butene were obtained using a 10 cm path length cell equipped with NaCl windows on a Beckman Instruments Model 4240 infrared spectrophotometer.

RESULTS AND DISCUSSION

Ion formation is initiated by a 10 ms electron beam pulse at approximately 5 eV. Dissociative electron attachment to ammonia produces H^- and NH_2^- both of which react with C_4H_8 isomers to form butenyl anions in Reaction (1). Subsequent irradiation with a cw CO_2

$$B^- + C_4H_8 \rightarrow C_4H_7^- + BH \qquad (1)$$

$$B = NH_2,\ H$$

laser results in loss of ion signal intensity due to multiphoton electron detachment. It is expected that absorption of only 3 or 4 photons is sufficient to cause detachment since $EA(CH_3CHCHCH_2) \approx 9$ kcal/mol.[19] The detached electrons remain in the ion trap but do not reattach to

NH_3 because the electron attachment cross section is sharply peaked at 5 eV.[20] In a typical experiment, $C_4H_7^-$ is formed via Reaction (1) for 100 ms in the absence of laser irradiation. Subsequent irradiation for 100 ms at 929 cm^{-1} and 30 W cm^{-2} results in loss of 50% or more of the ions. By varying the laser frequency while keeping all other experimental conditions the same, an infrared multiphoton electron detachment spectrum is obtained. Spectra obtained for these conditions are shown in Figure 1 for $C_4H_7^-$ derived from cis- and trans-2-butene. The spectra are qualitatively similar to each other with the maximum photodetachment yields occurring at the low frequency limit of the CO_2 laser (about 927 cm^{-1}). The yields in the case of the trans- precursor are significantly higher, however, at the high frequency limit (about 1085 cm^{-1}).

It would be interesting to compare our photodetachment spectra with the infrared absorption spectra of free butenyl anions. They have unfortunately not been reported, to our knowledge. Examination of the absorption spectra of 2-butenes (Figure 2) should provide a qualitative guide to the spectral differences one might expect between butenyl anion isomers. The 963 cm^{-1} band of trans-2-butene, for example, is more than three times as intense than its 975 cm^{-1} counterpart in cis-2-butene. Other differences in band shapes, positions and intensities are apparent in Figure 2. Thus while the photodetachment spectra of the butenyl anion isomers are expected to be somewhat alike, it would be surprising if they are so alike as the two spectra in Figure 1.

Without additional information, it would be difficult to draw any definite conclusions concerning the structures of the anions in Figure

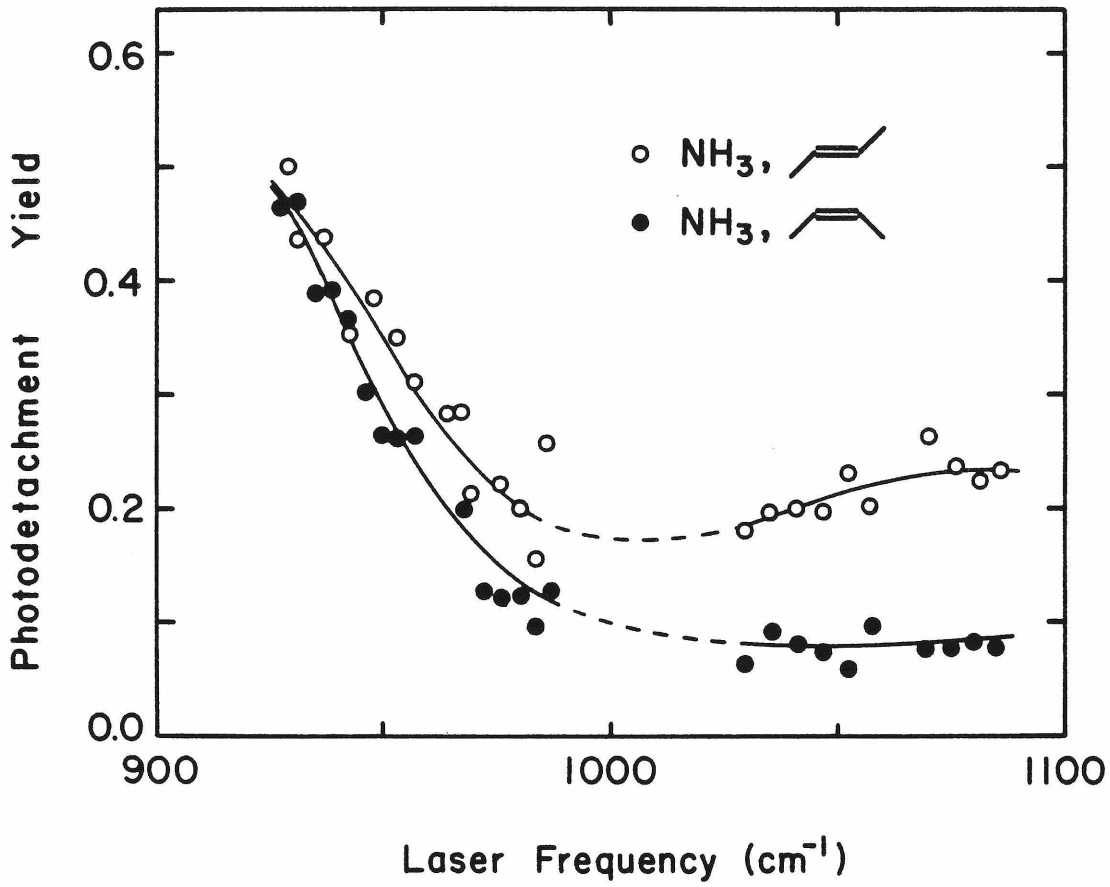

Figure 1. Infrared multiphoton electron detachment spectra of $C_4H_7^-$ produced by ionization of mixtures of ammonia with trans-2-butene (open circles) and cis-2-butene (solid points). Neutral pressures of ammonia and butene were 4.5 x 10^{-6} and 1.3 x 10^{-6} Torr in each case. A 100 ms ion formation period was followed by 100 ms of laser irradiation at 30 W cm^{-2} at each laser frequency.

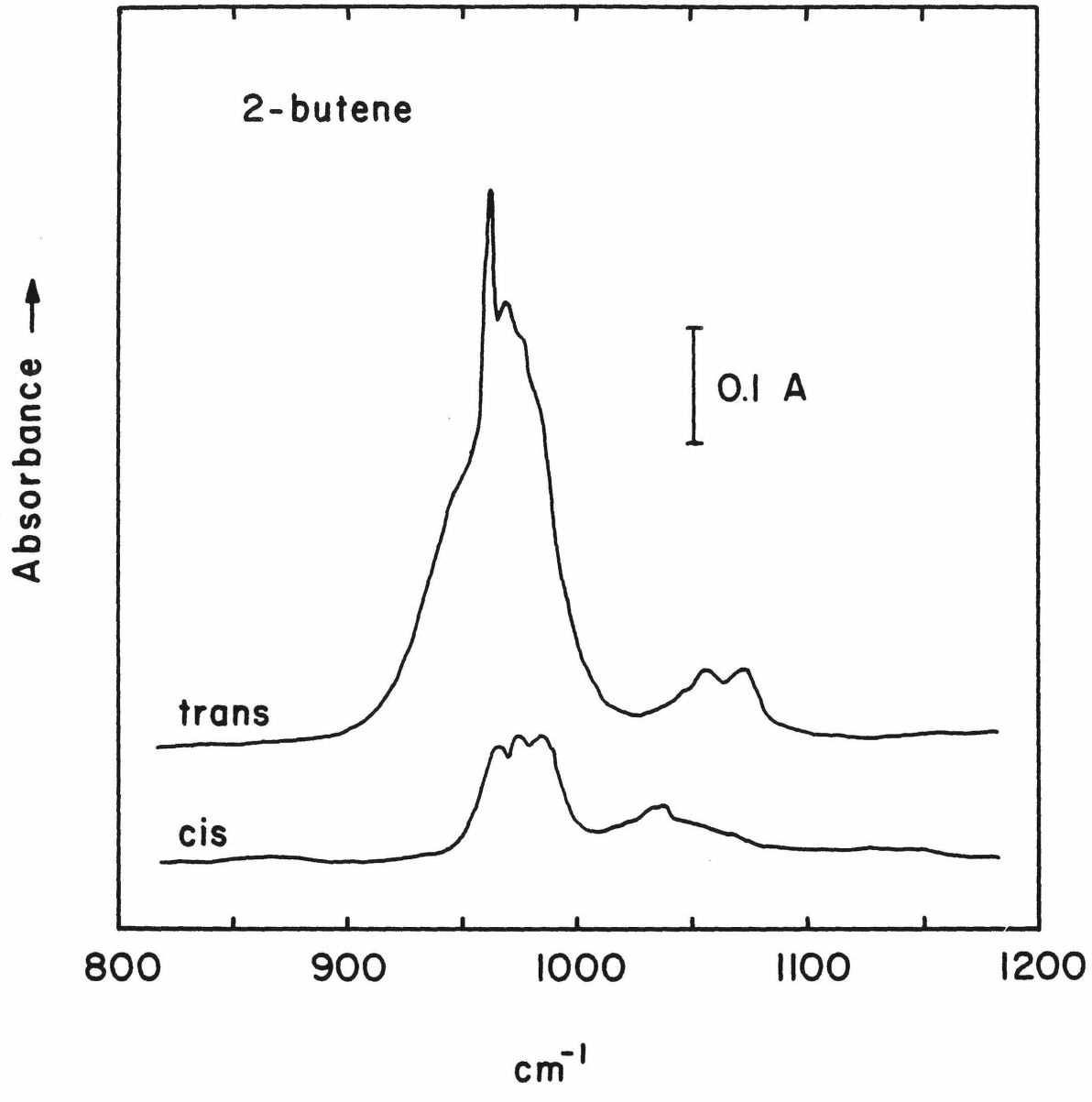

Figure 2. Infrared absorption spectra of neutral 2-butene isomers at 20 Torr. The path length of the gas cell is 10 cm. Spectra are plotted as absorbance vs. wave number so that the peak heights are proportional to the absorption cross sections. The maximum cross sections in this region for the cis and trans isomers are 1.6×10^{-20} cm^2 (975 cm^{-1}) and 7.5×10^{-20} cm^2 (963 cm^{-1}), respectively.

1. Fortunately, low power laser excitation affords the opportunity to examine the photodetachment rate as well as the total yield. The decay of $C_4H_7^-$ population with increasing laser irradiation period is shown in Fig. 3. Using cis-2-butene as the neutral precursor, the disappearance of $C_4H_7^-$ is exponential in time for irradiation at 929 and 1076 cm^{-1}. We conclude that all of the anions produced this way have the same phenomenological photodetachment cross section and with sufficiently long irradiation periods, 100% of the ions may be destroyed. The photodetachment cross section σ is defined as the first-order detachment rate constant divided by the laser photon flux.

If $C_4H_7^-$ is formed from trans-2-butene, very different behavior is observed. The disappearance of the ion signal is no longer a single exponential decay for 1076 cm^{-1} irradiation. Instead, 14% of the ions undergo rapid detachment with $\sigma = 30 \times 10^{21}$ cm^2 while the remaining 86% have a much lower cross section, comparable to $C_4H_7^-$ formed from cis-2-butene. The most likely explanation of these results is that proton abstraction from cis-2-butene forms exclusively the cis-butenyl anion whereas abstraction from trans-2-butene results in a mixture of 86% cis-$C_4H_7^-$ and 14% trans-$C_4H_7^-$.[20] Irradiation of the mixture at 929 cm^{-1} again results in a single exponential decay, suggesting that the cis and trans-butenyl anions have the same photodetachment cross section at this frequency, within experimental uncertainty.

These results are in good agreement with the spectra in Fig. 1. Since the cross sections for the cis and trans butenyl anions are the same at 927 cm^{-1}, the photodetachment yields for $C_4H_7^-$ from the

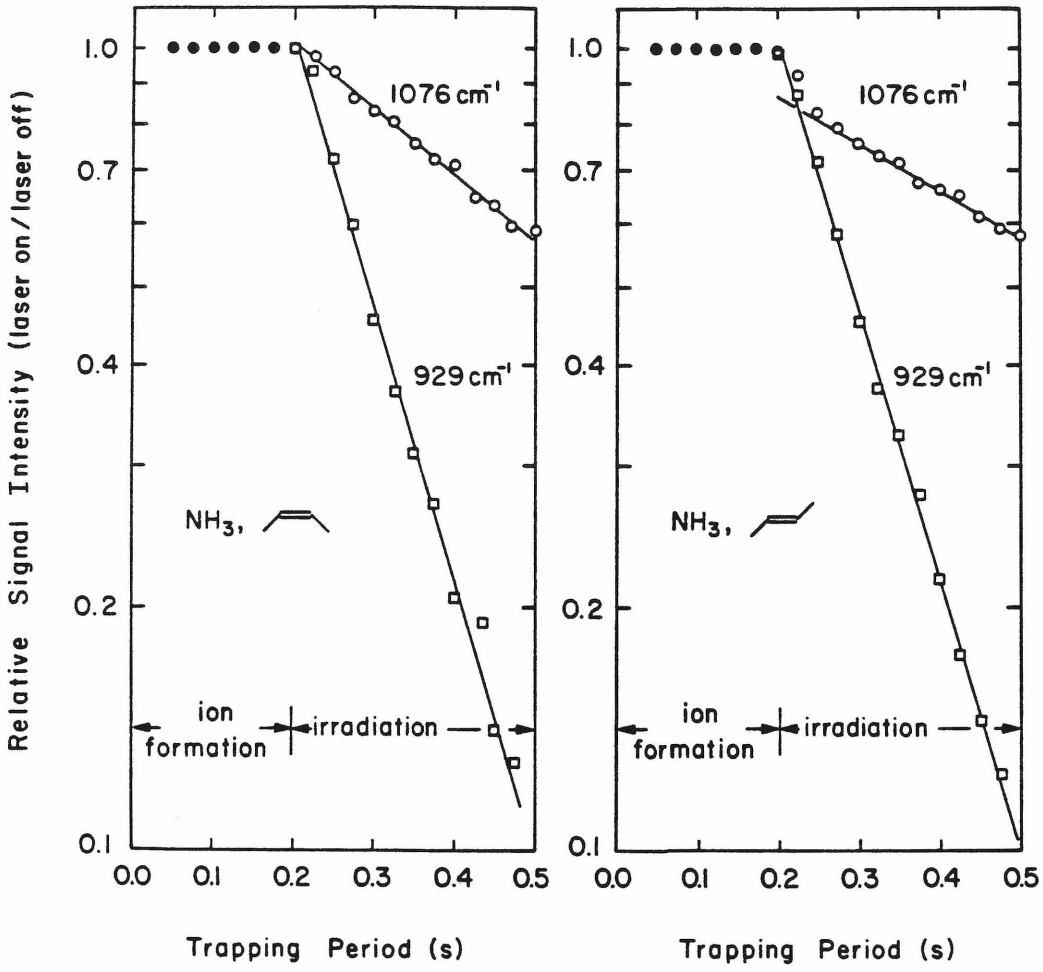

Figure 3. Semilogarithmic plots of relative $C_4H_7^-$ intensity versus trapping period. A 200 ms ion formation period precedes laser irradiation at 40 W cm^{-2}. On the left, decay of anions from cis-2-butene is shown for 929 and 1076 cm^{-1} irradiation. The respective phenomenological photodetachment cross sections (σ) are 3.9×10^{-21} and 1.0×10^{-21} cm^2. On the right, the corresponding data for the trans-2-butene precursor are shown. Decay of 929 cm^{-1} irradiation is homogeneous, with $\sigma = 3.6 \times 10^{-21}$ cm^2 but the 1076 cm^{-1} curve reveals that 14% of the ions decay with $\sigma = 30 \times 10^{-21}$ cm^2 while the remainder have $\sigma = 0.7 \times 10^{-21}$ cm^2. Neutral pressures of NH_3 and butene are 2.1×10^{-6} and 1.1×10^{-6} Torr, respectively, corresponding to a total ion-molecule collision rate of approximately 90 s^{-1}.

isomeric 2-butenes are the same at this frequency. At the high frequency end of the spectrum (around 1076 cm^{-1}), only about 8% of the cis-butenyl anions are destroyed, under the conditions of Fig. 1, whereas 98% of the trans-butenyl anions are destroyed as a result of their much larger cross section. The increase in photodetachment yield at 1076 cm^{-1} is limited to about 14% because only that fraction of the $C_4H_7^-$ population exists as the trans isomer.

For comparison, spectra of butenyl anions from two additional precursors have been obtained. Proton abstraction from 1-butene is expected to form either cis- or trans-butenyl anion. The spectrum in Figure 4 is again consistent with formation of a mixture of cis- and trans-butenyl anions, although only about 10% of the mixture is trans in this case. The results are consistent with the observation that 1-butene prefers the gauche conformation (75%) to the cis conformation (25%) at room temperature.[21] Also shown in Figure 4 is the spectrum of $C_4H_7^-$ resulting from proton abstraction from 2-methylpropene. As expected, this anion has a spectrum which is completely different from either cis- or trans-butenyl anions and probably exists as a stable 2-methylallyl anion.

Because collisions with both NH_3 and C_4H_8 neutrals occur on the time scale of these experiments it is difficult to tell if the compositions of cis-trans mixtures accurately reflect the nascent product distributions on formation of the butenyl anions by proton abstraction. It is possible, indeed likely, that some cis-trans isomerization is catalyzed by ion-molecule collisions before and during the laser irradiation period. Collisions with NH_3 would be expected to favor

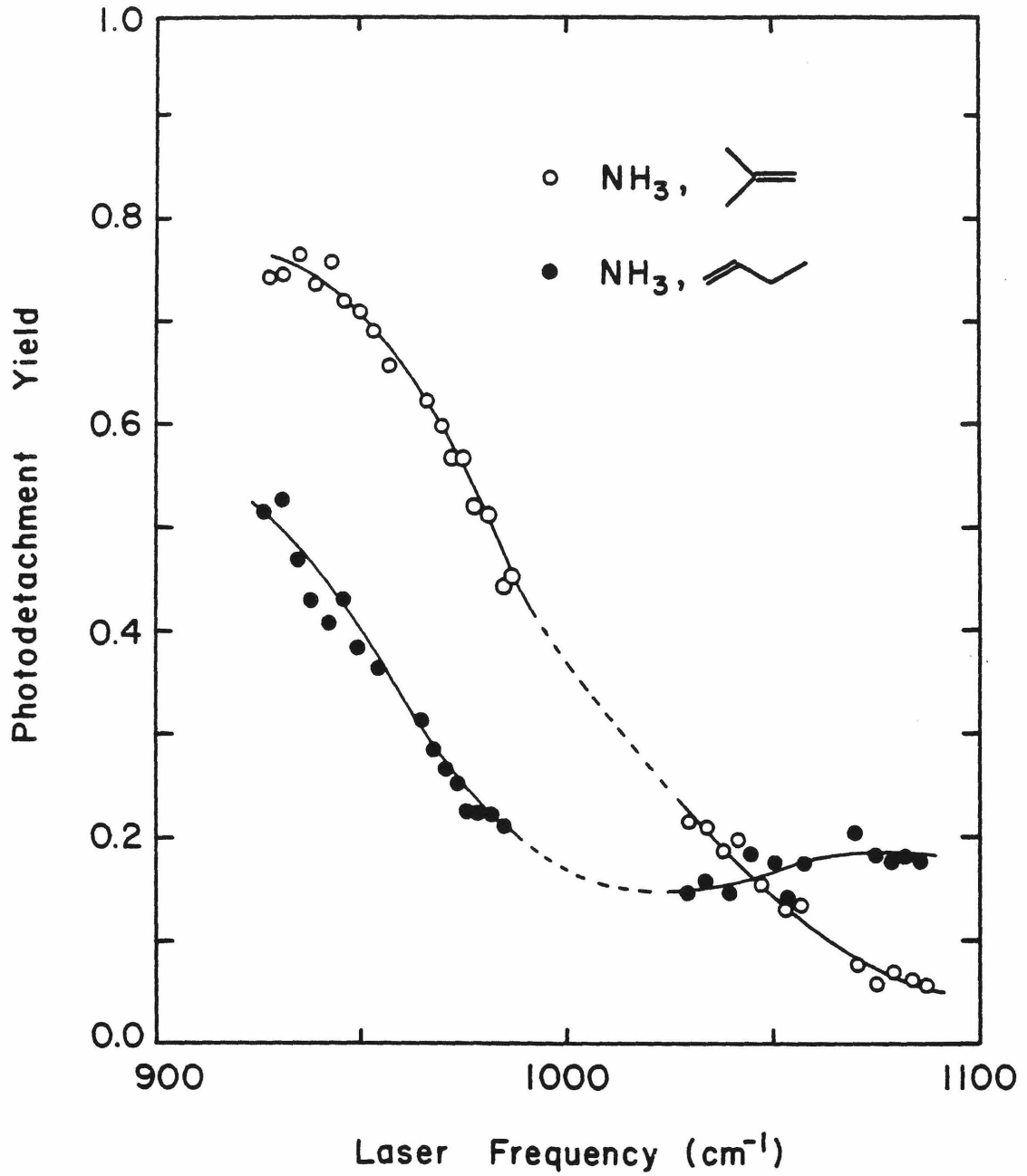

Figure 4. Infrared multiphoton electron detachment spectra of $C_4H_7^-$ produced by ionization of mixtures of ammonia with 2-methyl propene (open circles) and 1-butene (solid points). Neutral pressures of ammonia and butene were 3.0×10^{-6} and 1.2×10^{-6} Torr in each case. A 100 ms ion formation period was followed by 100 ms of laser irradiation at 30 W cm^{-2} at each laser frequency.

formation of the thermodynamically more stable isomer. Collisions with neutral butenes might give more of the isomeric butenyl anion corresponding to the structure of the neutral molecule than predicted for an equilibrium mixture because of the possibility of reactive proton transfer. In any case the data show that the cis-butenyl isomer is the kinetically favored product and is most likely the thermodynamically more stable 1-methylallyl anion. No information concerning the relative stabilities of 1-methylallyl and 2-methylallyl anions is available from these data since there is no apparent interconversion of these isomers and formation of 2-methylallyl anion from 2-methylpropene is characterized by a population of $C_4H_7^-$ with a homogeneous cross section for photodetachment.

It is interesting to note that although interconversion of cis and trans butenyl anions probably does occur during ion-molecule collisions, unimolecular isomerization by laser excitation is an unlikely process. The electron affinity of allylic anions is due in large part to the delocalization of the extra electron over three carbon centers. Interconversion of the cis and trans butenyl anions must involve rotation about one of the allylic C-C bonds, forcing the extra electron to be localized on a single carbon atom. This configuration would be expected to have zero (or very small) electron binding energy.[22] Since each absorbed photon deposits about 2.8 kcal/mol, it is unlikely that any anion would have enough energy to isomerize and still be stable with respect to electron detachment.

CONCLUSIONS

Low power infrared laser photodetachment of gas phase anions is a convenient method of distinguishing between anions with very similar isomeric structures. Monitoring detachment yield as a function of laser wavelength is useful when the spectra of the pure isomers are sufficiently distinct. Kinetic evaluation of the photodetachment rate provides additional information which is useful for evaluating spectra of isomeric mixtures. In this case the large difference in photodetachment cross sections at 1076 cm^{-1} allowed a quantitative determination of the composition of cis- and trans-butenyl anion mixtures. Since formation of the cis isomer is dominant in mixtures of ammonia with cis- or trans-2-butene, proton abstraction is judged to be a poor method of preparing trans-butenyl anion for chemical or photochemical study.

ACKNOWLEDGMENTS

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19. The electron affinity of C_4H_7 is estimated from the acidity of 2-butene, ΔH_a = 389 kcal/mol,[12] the allylic C-H bond energy of 1-butene, $D(C_4H_7\text{-}H)$ = 82.5 kcal/mol (Golden, D. M.; Benson, S. W. Chem. Rev. 1969, 69, 125) and the difference between the heats of formation of 1-butene and cis-2-butene, 1.7 kcal/mol.[8]

20. There is a possibility that the two different populations of $C_4H_7^-$ from trans-2-butene stem from different degrees of vibrational excitation. This is considered unlikely because similar effects would be expected using the cis precursor. Also, enhanced low power multiphoton excitation due to internal excitation has so far been documented only for ions with nine atoms or less (Woodin, R.L.;

Bomse, D. S.; Beauchamp, J. L. Chem. Phys. Lett. 1979, 63, 630. Thorne, L. R.; Beauchamp, J. L. J. Chem. Phys. 1981, 74, 5100. Wight, C. A.; Beauchamp, J. L. J. Am. Chem. Soc., to be submitted).

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22. The electron affinities of non-delocalized anions are very small. For example EA(CH_3) = 1.8 kcal/mol (Ellison, G. B.; Engelking, P. C.; Lineberger, W. C. J. Chem. Phys. 1976, 65, 4323).

CHAPTER V

Infrared Laser Photodetachment of Electrons from Vibrationally Excited Allyl Anions.

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Abstract:

Infrared laser photodetachment of allyl anions has been investigated using the techniques of ion cyclotron resonance spectroscopy. Facile detachment of vibrationally excited anions occurs with a phenomenologically defined cross section $\sigma^* = 6.5 \times 10^{-20}$ cm^2 using a low power cw CO_2 laser. Photodetachment from vibrationally relaxed anions also occurs, but with a much lower cross section $\sigma = 6.3 \times 10^{-23}$ cm^2. When fluoride ion reacts with allyltrimethylsilane, 29% of the nascent allyl anions are vibrationally excited. The predominant relaxation mechanism is by radiative emission with a measured rate constant of 53 s^{-1}. The level of vibrational excitation probed is believed to be approximately 12.7 kcal/mol, the adiabatic electron affinity of allyl radical. The photodetachment yield from vibrationally excited allyl anions is only weakly dependent on laser wavelength in the 10 μm region and a photodetachment spectrum is presented.

INTRODUCTION

Although infrared laser induced chemical reactions[1] have received much attention since the development of the CO_2-TEA laser, application of these techniques to gas phase ions has been relatively recent. We have previously demonstrated that multiphoton dissociation[2] of positive ions and multiphoton electron detachment[3, 4] of negative ions may be induced by a low power cw CO_2 laser merely by isolating the ions in a collision free environment for several hundred milliseconds during laser irradiation. Ion cyclotron resonance spectroscopy has proven to be a valuable technique for formation, storage and detection of positive and negative ions for these studies.

The intimate coupling between vibrational and electronic degrees of freedom which is necessary to observe multiphoton electron detachment makes these studies particularly interesting. The process may be thought of as a type of inverse electronic relaxation in that a vibrationally "hot" anion undergoes an electronic transition (detachment) resulting in a relatively "cool" neutral molecule. Brauman and coworkers first reported infrared multiphoton electron detachment with a pulsed CO_2 laser in their studies[5, 6] of several delocalized anions. Using the low power cw laser, we have used the technique to distinguish between isomeric anions on the basis of their infrared spectra.[3] These spectra are obtained by monitoring infrared photodetachment yields as a function of the wavelength of the exciting laser. Simons has recently presented an interesting theoretical analysis of vibrationally driven electron detachment processes.[7]

In this paper, we report the results of infrared laser photodetachment of electrons from allyl anions. The observed photodetachment

kinetics show that a substantial fraction of the population is vibrationally excited. An infrared photodetachment spectrum of these excited anions is given. By varying the laser intensity and by systematically delaying the start of laser irradiation relative to the ion formation period, we have extracted the cross section for laser photodetachment of vibrationally excited anions and the rate constant for radiative relaxation. In the discussion section we compare the results with the relaxation rate constant calculated using the method outlined by Dunbar[8] in which infrared radiative emission rate coefficients are obtained from integrated infrared absorption intensities. The very high apparent degree of vibrational excitation in allyl anions is discussed in terms of the ion molecule reactions which produce them.

EXPERIMENTAL SECTION

The theory, techniques and instrumentation of trapped ion ICR spectroscopy have been described in detail elsewhere.[9,10] The ICR cell has been modified for photochemical studies by replacing one of the source drift plates with a 92% transmittance wire mesh. The unfocused laser beam enters the vacuum enclosure through a polished NaCl window, passes through the mesh and the ion trapping region and is reflected off the rear drift plate back out the window after a second pass through the ion trap. The optical configuration is illustrated in Figure 1. Power from the line-tunable cw CO_2 laser (Apollo Model 550A) is measured using a Laser Precision Corp. pyroelectric radiometer (Model RkP-345) and the beam shape is monitored using an Optical Engineering Model 22A thermal imaging plate. Wavelength calibration is performed using an Optical Engineering Model 16A spectrum analyzer.

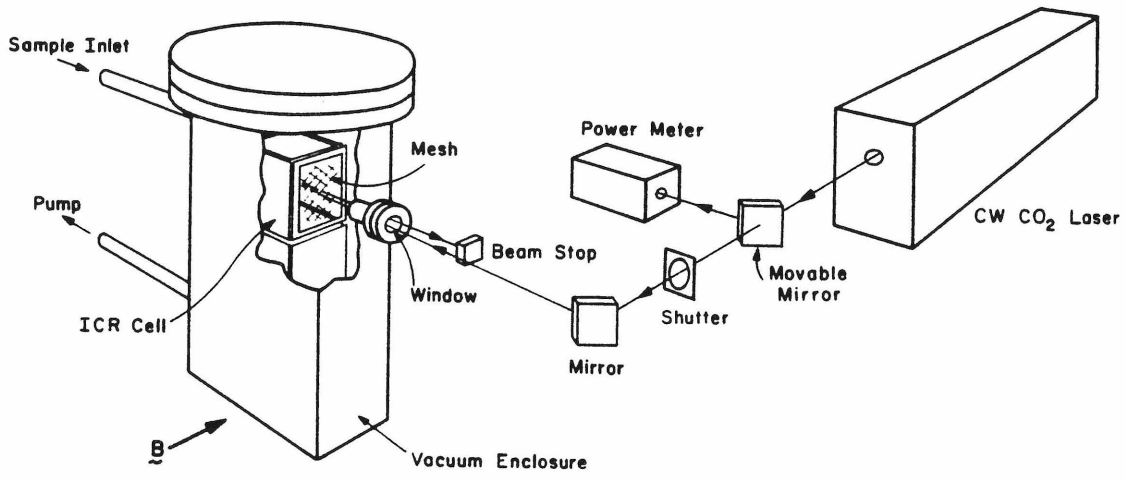


FIG. 1. Schematic diagram of the optical configuration for photochemical ICR studies. The vector $\underset{\sim}{B}$ indicates the orientation of the magnetic field (magnet not shown).

An electronically controlled mechanical shutter (Uniblitz Model 225LOA14X5) is used to irradiate the ions only during alternate trapping cycles. The corresponding ion intensities (laser on and laser off) are monitored and averaged by a two channel boxcar integrator. These signals are then processed in a straightforward fashion to yield photodetachment yields even in the presence of ion loss due to diffusion and reaction. Additional details are presented elsewhere.[11]

Nitrogen trifluoride, ammonia, propene, allyltrimethylsilane and nitrogen were obtained from commercial sources and were used without further purification except for degassing at liquid nitrogen temperature. Pressures of neutral gases were measured using a Schulz-Phelps type ionization gauge which was calibrated for each gas at higher pressure using an MKS Instruments Baratron Model 90H1-E capacitance manometer. It is estimated that absolute pressure determinations are within ± 20% using this method.

The infrared spectrum of propene at 50 Torr was obtained using a 10 cm gas cell with NaCl windows in a Beckman Model 4240 infrared spectrophotometer.

RESULTS

Ion Formation

A 10 ms pulse of low energy electrons produces fluoride ion by dissociative electron attachment of NF_3. Subsequent reaction with allyltrimethylsilane provides an efficient method of producing allyl anion

$$F^- + (CH_3)_3Si(C_3H_5) \rightarrow C_3H_5^- + (CH_3)_3SiF \qquad (1)$$

for photochemical study.[12] Although the electron affinity of C_3H_5

(0.55 eV) is much less than that of a fluorine atom (3.45 eV), the driving force for this reaction is provided by the strong (154 kcal/mol) silicon-fluorine bond.[12] Reaction (1) is estimated to be exothermic by 14 kcal/mol and the measured rate constant is 9×10^{-10} cm^3 molecule^{-1} s^{-1}.

Another method of forming allyl anion is by proton abstraction from propene by a strong anionic base. Dissociative electron attachment

$$B^- + CH_3CHCH_2 \rightarrow C_3H_5^- + BH \qquad (2)$$

of 5.1 eV electrons to ammonia produces H^- and NH_2^-, both of which react with propene forming allyl anion. Reaction (2) is exothermic by 9.6 and 8.8 kcal/mol for these bases, respectively.[13]

Infrared Laser Photodetachment

When exposed to laser radiation in the 10 μm region a decrease in allyl anion signal intensity is observed, corresponding to electron detachment. Figure 2 indicates that the decrease for $C_3H_5^-$ produced by Reaction (1) occurs mainly at short times corresponding roughly to the ion formation period. At longer times, detachment is quite slow, even at laser intensities in excess of 100 W cm^{-2}. This behavior is consistent with the formation of at least two different populations of allyl anion with widely varying cross sections for photodetachment. The most likely cause of this difference is excess internal energy which lowers the number of infrared photons which are needed to reach the electron detachment threshold. Production of allyl anions via the less exothermic Reaction (2) results in yields which are approximately 70% of those obtained with Reaction (1) under similar conditions, although qualitatively the behavior is the same (Figure 2).

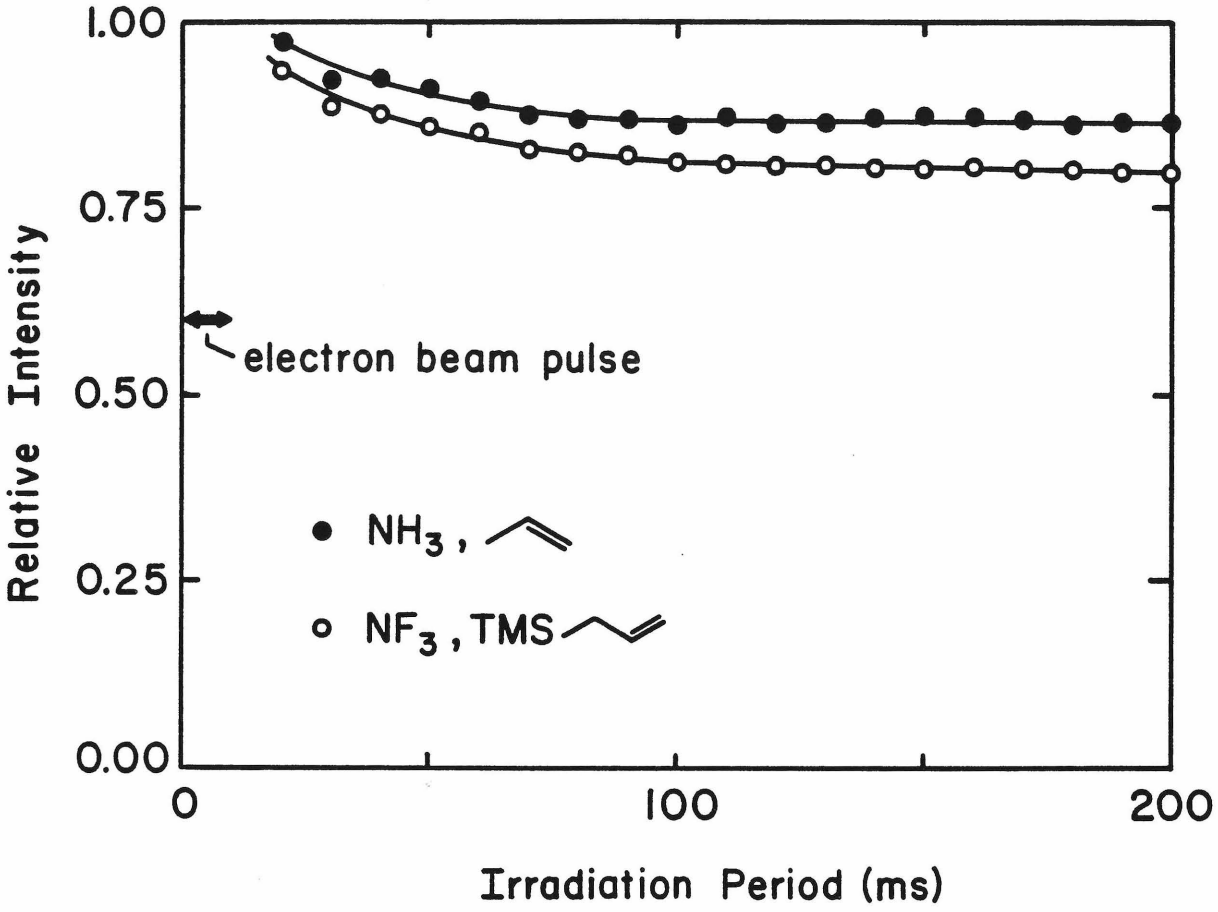


FIG. 2. Decay of allyl anion signal intensity as a function of laser irradiation period. Laser intensity is 40 W cm^{-2} at 942.4 cm^{-1}. Open circles indicate allyl anion produced by Reaction (1) with $P(NF_3)$ = 5.1 x 10^{-7} Torr, P(allyltrimethylsilane) = 1.4 x 10^{-6} Torr. Solid points indicate allyl anion produced by Reaction (2) with $P(NH_3)$ = 3 x 10^{-6} Torr, $P(C_3H_6)$ = 1.5 x 10^{-6} Torr. Ion formation is initiated by a 10 ms electron beam pulse and production of allyl anion is $>95\%$ complete by 100 ms in each case.

It is expected that electrons detached from allyl anions may reattach to NF_3, eventually regenerating allyl anion. The shape of the decay curves in Figure 2 is not due to formation of a photostationary state, however, since delaying the start of laser irradiation until after ion formation is complete results in a drastic decrease in the photodetachment yield. In addition, reattachment to NH_3 is highly unlikely since the cross section for dissociative attachment is sharply peaked at 5.1 eV.[14]

Since irradiation of the ions after the ion formation period results in only very slow electron detachment, rapid relaxation of vibrationally excited ions must be occurring. Addition of propene as a buffer gas results in only a modest decrease in the photodetachment yield, however, and addition of N_2 actually increases the photodetachment yield slightly (Figure 3). Clearly, radiative emission is the dominant relaxation mechanism under the low pressure conditions of Figure 2.

In order to estimate the radiative relaxation rate, an experiment was performed in which production of $C_3H_5^-$ was stopped by continuous double resonance ejection of F^- from the ion trap beginning 50 ms after the electron beam pulse. Laser irradiation was limited to a 50 ms period following the start of F^- ejection. By systematically increasing the delay between the start of F^- ejection and the start of laser irradiation it was found that the detachment yield decreased exponentially to a constant value (Figure 4) corresponding to the slow detachment rate. From this exponential decay, a radiative relaxation rate of 53 s^{-1} is estimated. The photodetachment yield at long times is constant and gives a photodetachment cross section of $\sigma = 6.3 \times 10^{-23}$ cm^2 for vibrationally relaxed allyl anion. The cross section is defined as the photo-

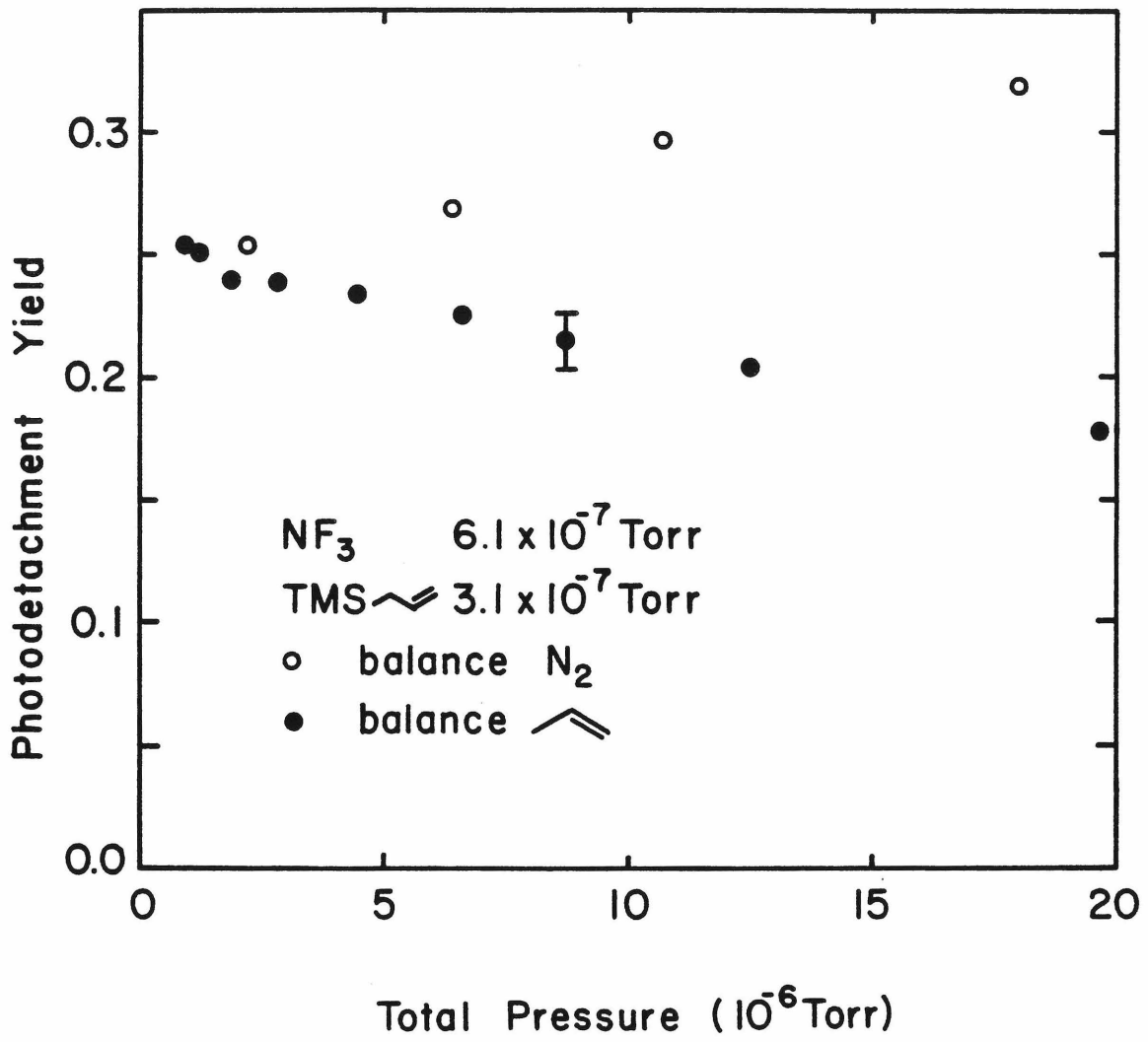


FIG. 3. Photodetachment yield of allyl anion vs. neutral gas pressure. Irradiation is for 200 ms beginning at the start of the 10 ms electron beam pulse. Laser intensity is 90 W cm^{-2} at 942.4 cm^{-1}. Use of N_2 as the buffer gas results in an increase in photodetachment yield (open circles) whereas a decrease is observed using propene (solid points). The error bars indicate the estimated uncertainty for each point.

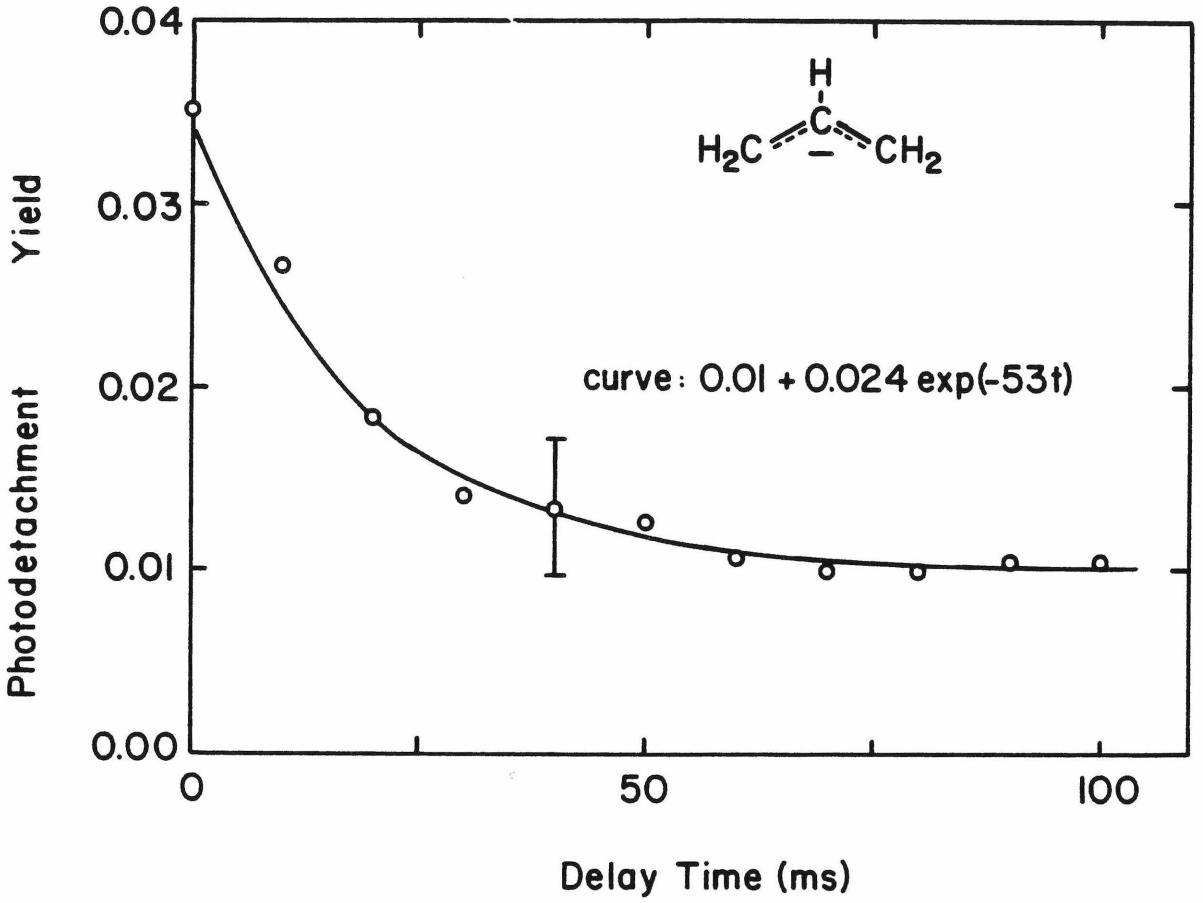
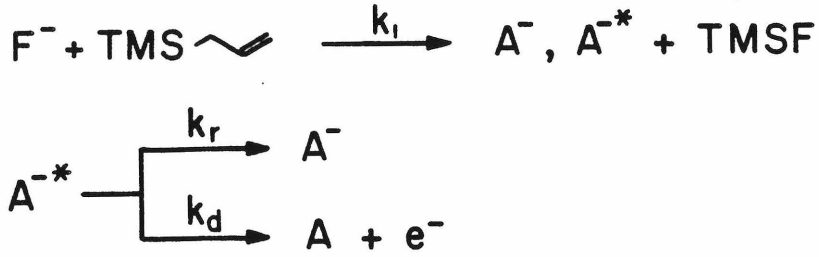


FIG. 4. Photodetachment yield as a function of relaxation time for allyl anions. A 10 ms electron beam pulse is followed by a 40 ms ion formation period after which fluoride ion is ejected from the ion trap, halting the production of $C_3H_5^-$. The start of a 50 ms irradiation period is delayed with respect to the start of F^- ejection. Detection of $C_3H_5^-$ immediately follows the irradiation period in all cases. Laser intensity is 60 W cm^{-2} at 948 cm^{-1}. Neutral pressures of NF_3 and allyltrimethylsilane are 5.1 x 10^{-7} and 1.5 x 10^{-6} Torr, respectively. The estimated uncertainty is indicated by the bars at 40 ms delay.

detachment rate constant divided by the photon flux of the laser.

A determination of the photodetachment cross section for vibrationally excited ions requires a closer examination of the overall kinetics of the detachment process. In the simplest treatment (Scheme I) ion formation is assumed to result in two populations of allyl anion corresponding to relaxed (A^-) and vibrationally excited (A^{-*}) ions.

Scheme I



Vibrationally excited ions may then either relax to A^- or, in the presence of laser irradiation they may undergo electron detachment to form allyl radical (A). The population of A^{-*} as a function of time is given by Eq. (3), where k_1 is the pseudo first-order rate constant (which includes

$$A^{-*}(t) = \frac{f k_1 F_0}{k_r + k_d - k_1} \left\{ \exp[-k_1 t] - \exp[-(k_r + k_d)t] \right\} \quad (3)$$

the concentration of allyltrimethylsilane), F_0 is the number of fluoride ions originally produced and f is the fraction of those ions which react to form vibrationally excited allyl anions. The number of allyl radicals produced is then given by Eq. (4). While this expression is a bit

$$A(t)=\frac{k_d k_1 f F_0}{(k_r+k_d-k_1)k_1(k_r+k_d)}\left\{k_r+k_d-k_1+k_1\exp[-(k_r+k_d)t]-[k_r+k_d]\exp[-k_1 t]\right\} \quad (4)$$

cumbersome to deal with directly, it simplifies at long times $[t \gg (k_1)^{-1}, (k_r)^{-1}]$ to Eq. (5). Substituting $\Phi\sigma^*$ for k_d where Φ is the

$$A(t\rightarrow\infty) = \frac{k_d F_0 f}{k_r + k_d} \quad (5)$$

photon flux and σ^* is the cross section for photodetachment of vibrationally excited anions, and putting Eq. (5) in terms of experimental observables, we obtain Eq. (6) where A^- and A_0^- are the allyl anion

$$\frac{A_0^-}{A_0^- - A^-} = \frac{k_r}{f\sigma^*\Phi} + \frac{1}{f} \quad (6)$$

intensities at long times in the presence and absence of laser radiation, respectively. A plot of the left hand side of Eq. (6) vs. Φ^{-1} is given in Figure 5. The y-intercept yields f = 0.29 and the slope gives $k_r(\sigma^*)^{-1} = 8.21 \times 10^{20}$ cm^{-2} s^{-1}. Using $k_r = 53$ s^{-1} from Figure 4, we obtain $\sigma^* = 6.5 \times 10^{-20}$cm^2. In our analysis we have ignored the fact that some ion loss is due to slow photodetachment of relaxed anions; however, this is not expected to introduce a significant error in the analysis since $\sigma^*/\sigma = 1.0 \times 10^3$.

Finally, the infrared photodetachment yield exhibits very little dependence on the wavelength of the laser in the 10μm region (Figure 6). Since photodetachment occurs mainly from vibrationally excited allyl anions, the spectrum is actually that of the excited anions and could be quite different from that of ground state allyl anions. Photodetachment with a pulsed CO_2 laser has also been reported to have only a modest

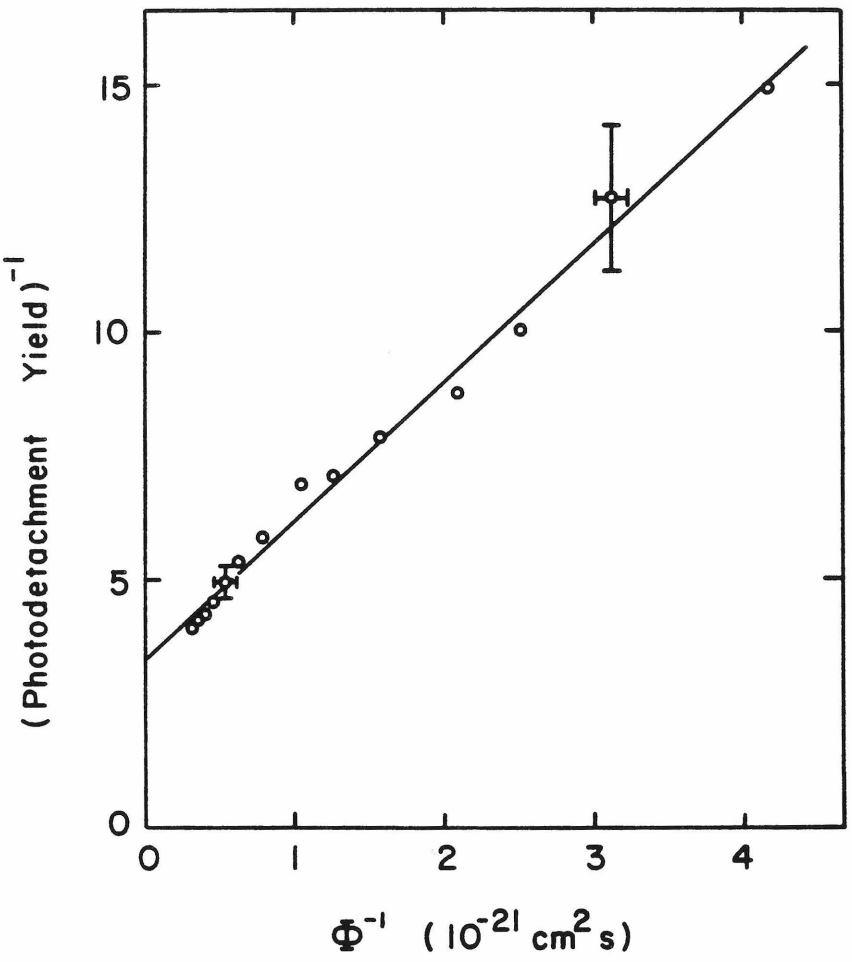


FIG. 5. The reciprocal of the photodetachment yield (LHS of Eq. 6) plotted vs. the reciprocal of laser photon flux yields the least squares fit shown. The slope is 2.79 x 10^{21} cm^{-2} s^{-1} and the y-intercept is 3.4. The 200 ms irradiation period begins at the initiation of ion formation. Laser intensity is varied from 60 to 4.5 W cm^{-2} at 948 cm^{-1}. Neutral pressures of NF_3 and allyltrimethylsilane are 5.1 x 10^{-7} and 6.9 x 10^{-7} Torr, respectively.

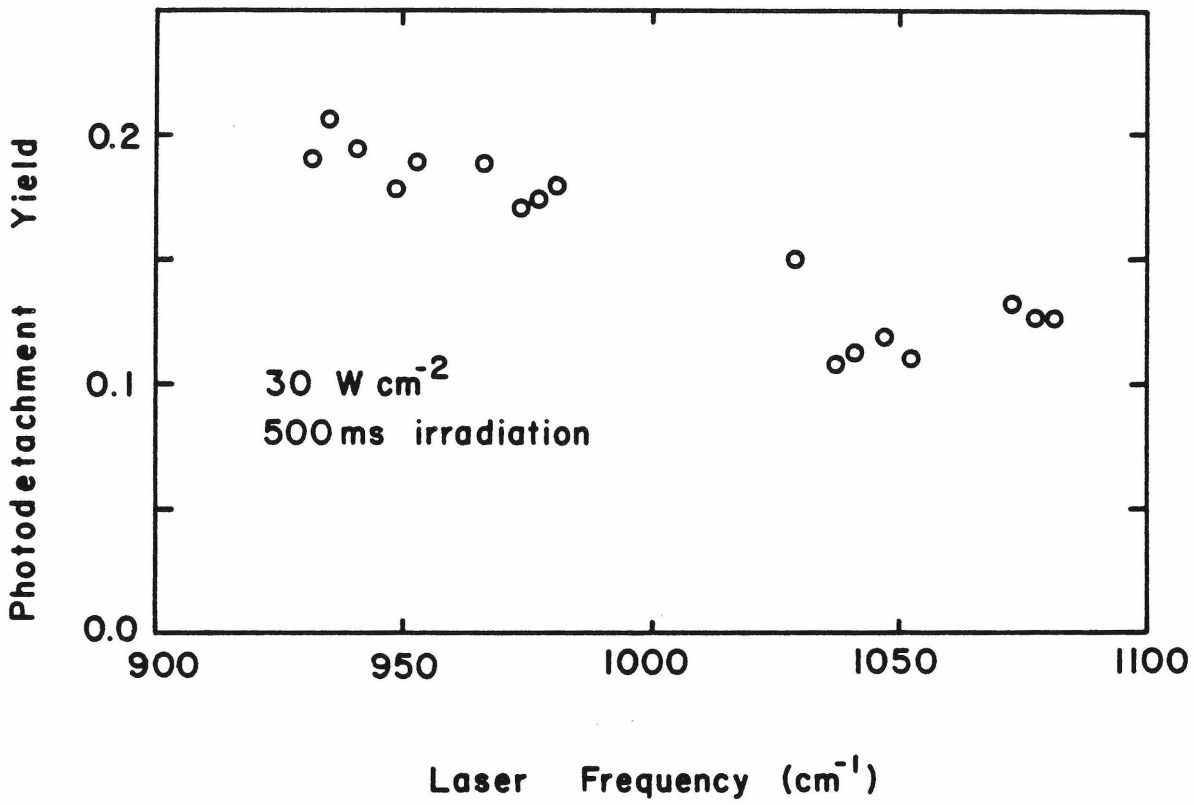


FIG. 6. Infrared photodetachment spectrum of vibrationally excited allyl anions obtained by monitoring the detachment yield as a function of CO_2 laser frequency. The 500 ms irradiation period begins at the initiation of ion formation. Laser intensity at each point is 30 W cm^{-2}. Neutral pressures of NF_3 and allyltrimethylsilane are 5.1 x 10^{-7} and 1.7 x 10^{-7} Torr, respectively.

wavelength dependence.[6]

DISCUSSION

How quickly do ions come into thermal equilibrium in an ICR spectrometer? This question, which has also been raised in conjunction with other methods of studying ion-molecule reactions, remains for the most part unanswered.[10] Although internal energy in ions is known to affect reaction rates or branching ratios in many cases,[15-17] there are very few methods which are well suited to probing vibrational excitation in ions and analyzing their relaxation mechanisms.[18,19] This lack of data makes it difficult to predict if vibrational excitation is likely to introduce errors in the determination of free energies from what is assumed to be a process at equilibrium. The observation of an ion molecule reaction in ICR experiments is generally taken to be good evidence that the reaction is not substantially endothermic. Similarly, scales of acid-base properties of molecules and ions have been based on equilibrium measurements of ion-molecule reactions which are nearly thermoneutral. Since vibrational excitation can be important in determining reaction rates, particularly for endothermic processes, errors in the thermodynamic values may result in studies where "hot" ion populations are present. In a recent study, the rate constant of an endothermic ion molecule reaction was increased by over three orders of magnitude as a result of infrared laser excitation of the ion.[20]

In this study, we have shown that for allyl anion, infrared laser photodetachment is a rather sensitive probe of vibrational excitation since the cross section for electron detachment is increased by three orders of magnitude compared with relaxed ions. Increasing the pressure

of neutral buffer gases has only a modest effect on the photodetachment yield, indicating that collisional deactivation is not important at low pressures. Further evaluation of collisional effects, however, is complicated by the observation that the yields increase slightly with the addition of nitrogen as the buffer gas. Although it is still not well understood, collisional enhancement of multiphoton dissociation[21] and multiphoton electron detachment[4] rates has been reported in other studies using low power laser excitation. At the highest buffer gas pressures used in this study, the collision rates are in excess of 600 s^{-1}, much faster than the measured radiative rate of 53 s^{-1}. Thus even though enhancement processes compete with collisional deactivation, we are left with an almost inescapable conclusion that collisions are not very effective for removing vibrational energy from allyl anion. This is in contrast to most observations in which addition of a buffer gas removes much of the energy from an excited ion in just a few collisions.[19] The operational definition of relaxation in most of these studies has been no further change in ion molecule reaction rates with increasing buffer gas concentration.

Since radiative stabilization of ions may be important for other ions as well as allyl anion, it is useful to be able to predict radiative relaxation rates. One method for estimating infrared radiative stabilization rates has been advanced by Dunbar.[8] Briefly, the integrated absorption intensities from an ordinary infrared spectrum may be related to the Einstein A coefficients for spontaneous emission from vibrational modes. By utilizing tabulated thermodynamic heat content functions or by direct calculation using statistical mechanics, a given internal energy is associated with an internal temperature which characterizes the extent of excitation within each vibrational mode. Free exchange of energy

between vibrational modes is assumed. By summing the properly weighted emission rates from each state, the total radiative emission rate is calculated as a function of vibrational energy. Because infrared spectra and vibrational frequencies are not available for most ions, band intensities and frequencies must be estimated from closely related neutral molecules. Spontaneous emission coefficients appropriate for allyl anion (Table I) were obtained from the infrared spectrum of propene and the vibrational frequencies for allyl anion (Table II) were estimated from the vibrational assignments for propene.[22] The resulting calculation of radiative relaxation rate vs. energy is given in Figure 7. Although the present experiment gives no direct information concerning what constitutes an "excited" anion or a "relaxed" anion, it is likely that the relaxation rate of 53 s^{-1} obtained from the data in Figure 4 is appropriate to the region around 12.7 kcal/mol, the adiabatic electron affinity of allyl radical. Anions with energies greatly in excess of this value would be expected to undergo autodetachment on the time scale of this experiment and anions with less than 10 kcal/mol require more than a single infrared photon to reach the adiabatic detachment threshold. Clearly the calculation has grossly underestimated the relaxation rate in this case. Jasinski and Brauman have recently investigated vibrational relaxation of CF_3O^- and report a radiative rate of 20 s^{-1}.[23] No theoretical estimate of this value was made.

Additional experimental data for other systems will probably be required to determine if the failure of the model occurs in other ionic systems and if so, how the method may be improved to give accurate predictions. Possibly a major source of error is the use of infrared

Table I. Estimated Infrared Spontaneous Emission Rate Coefficients for Allyl Anion[a]

cm^{-1}	$A(s^{-1})$
930	5.84
1440	5.71
1650	4.35
1825	1.17
2950	110.0

[a]Calculated using the infrared spectrum of propene

Table II. Estimated Vibrational Frequencies of Allyl Anion[a]

3090 cm^{-1}	1419 cm^{-1}	1150 cm^{-1}
3036	1378	991
2992	1298	912
2954	1229	700
2933	1200	578
1443	1172	578

[a]Estimated using vibrational assignments for propene (ref. 22) and adjusting some frequencies to reflect loss of a proton.

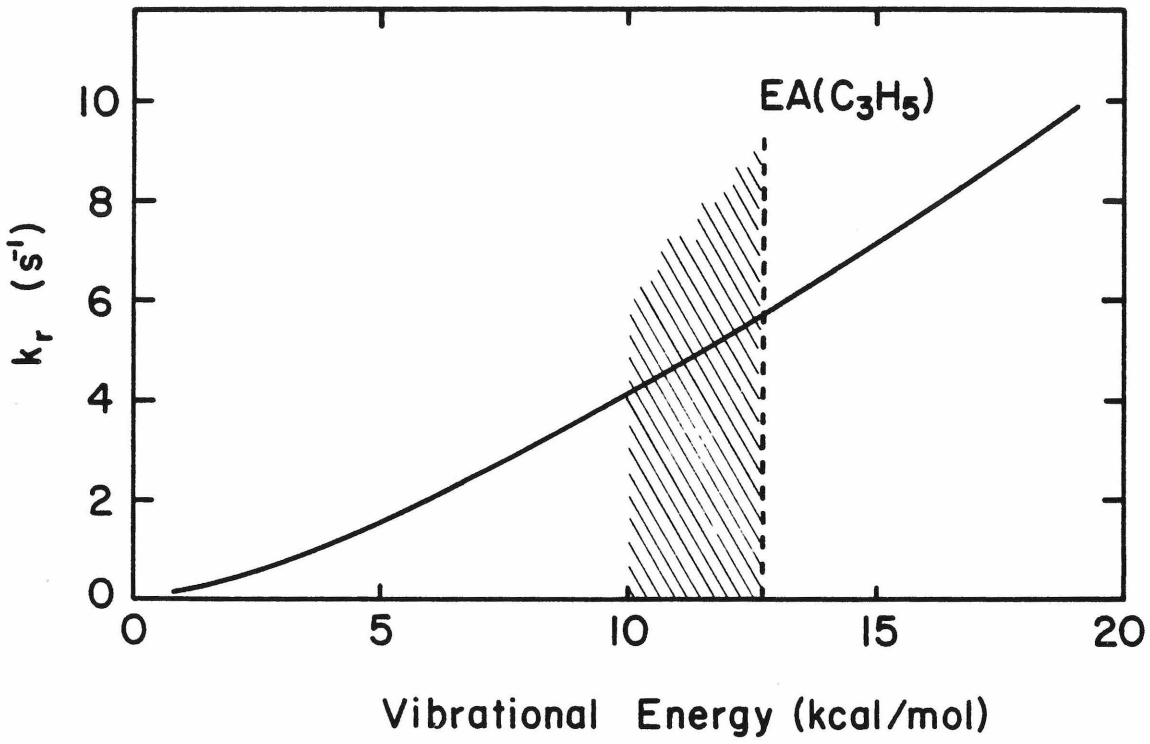


FIG. 7. Calculated radiative relaxation rate as a function of internal energy of allyl anion. The calculation follows the procedure outlined in ref. 8 using integrated band intensities from the gas phase infrared spectrum of propene. The shaded area represents allyl anions whose internal energy would exceed the adiabatic electron affinity of allyl radical by the absorption of a single 945 cm^{-1} photon.

spectra of neutrals to estimate transition oscillator strengths in ions. It may be that methylene twisting in allyl anion, for example, is accompanied by a high degree of charge localization in the normally delocalized anion. The resulting large change in dipole moment could lead to a much larger emission rate compared with the analogous motion in propene.

The suggestion above that the operational definition of "vibrationally excited" is approximately 10-13 kcal/mol deserves additional comment. The distinction between excited and relaxed is based on the assumption that while absorption of one photon is straightforward, absorption of two or more photons is expected to be more difficult. The density of vibrational states in allyl anion (Figure 8) is quite low for $E \leq 10$ kcal/mol. By comparison, vibrational state densities for ions which undergo facile multiphoton excitation of thermal energies are usually in excess of 1000 per cm^{-1} at this level of excitation.[24] The normally large density of states provides a mechanism by which energy may be channeled out of a "pumped" vibrational mode and into the other vibrational modes (the molecular heat bath). For molecules with low vibrational state densities, significant energy mismatches may prevent efficient transfer under collision-free conditions. At least part of the observed collisional enhancement of photodetachment yields may be due to increased intramolecular energy flow at low energies. For allyl anion, a two photon channel may be opening up at high pressures so that a greater fraction of the population is susceptible to laser photodetachment.

If we accept the hypothesis that up to 29% of allyl anions undergo

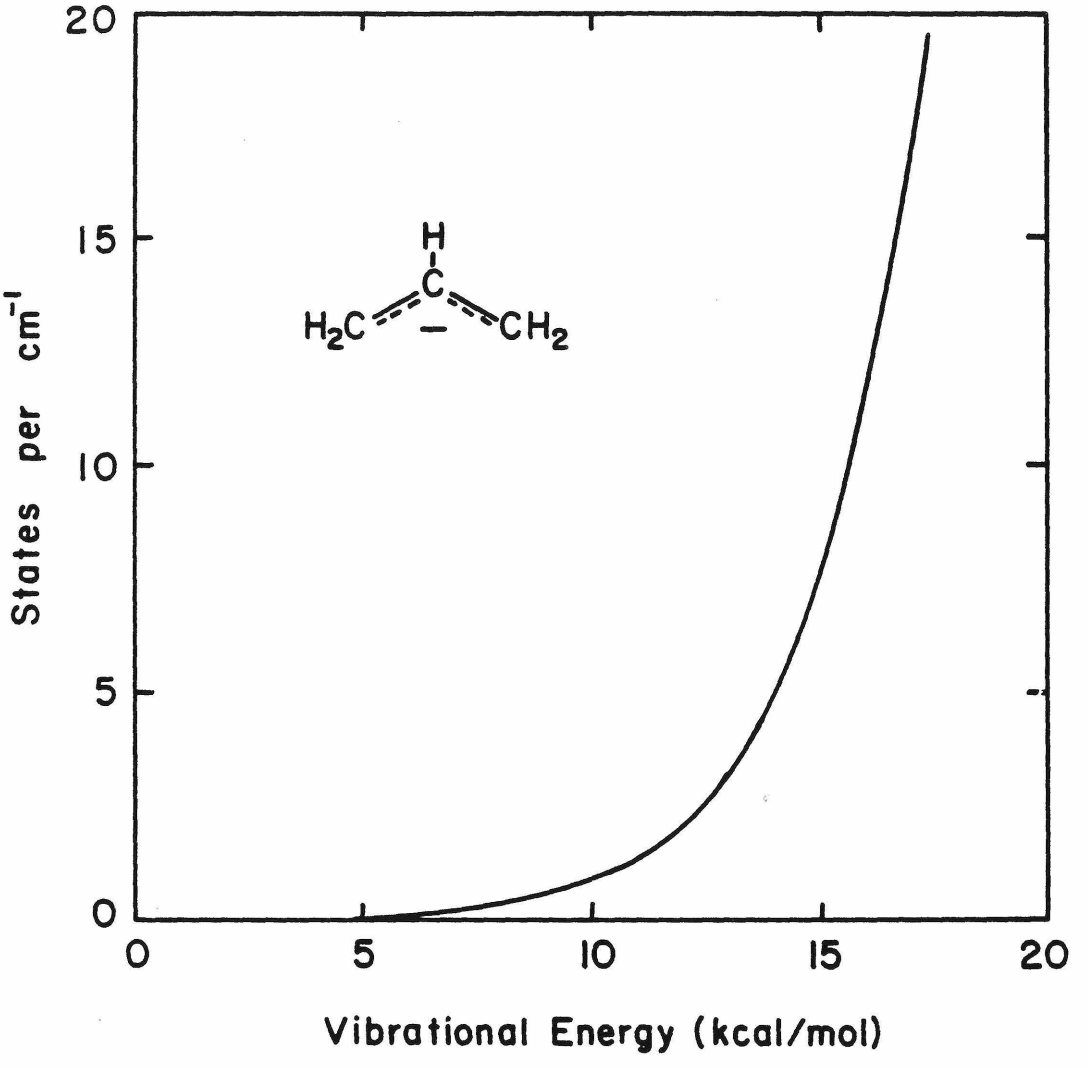


FIG. 8. Estimated vibrational state density for allyl anion calculated using the Whitten-Rabinovitch approximation. Vibrational frequencies for allyl anion were estimated from those of propene and are given in Table II.

single photon electron detachment, then we are faced with the task of explaining how such a great fraction of the energy released in Reactions (1) and (2) appears as vibrational energy in allyl anion. Statistical theories[25, 26] predict that most of the 14 kcal/mol in Reaction (1) will appear as vibrational excitation in $(CH_3)_3SiF$. The actual energy distribution, however, depends on the details of the reaction potential surface. Farneth and Brauman have suggested that reaction potential barriers are responsible for unusually slow proton transfer rate constants observed for several delocalized anions including benzyl anion.[27] The barriers are thought to arise partly from a loss of resonance energy in the transition state due to a requirement for charge localization. If an analogous situation exists in the transition state for Reaction (1), most of the resonance energy of allyl anion would be expected to appear as vibrational energy in the anion. Similar behavior has been reported in the case of benzyl radical. Hydrogen atom abstraction from toluene by fluorine atoms produces vibrationally and rotationally excited HF but the 11.2 kcal/mol resonance energy of benzyl radical remains in the radical as vibrational excitation.[28] On the basis of these observations it is not unreasonable to expect a large fraction of the excess energy in Reaction (1) to appear as vibrational excitation in allyl anion. A similar argument is made in the case of Reaction (2) and although the exothermicity is less than 10 kcal/mol, some excess internal energy may be present in NH_2^- as a result of dissociative electron attachment to NH_3 at 5.1 eV.

Infrared laser photochemistry may be an important tool for study-

ing vibrational excitation in ions. Numerous examples have now been reported in which large molecules ($\geq$ 9 atoms) have absorbed many photons to reach photodetachment or photodissociation thresholds.[24] In these cases the thermal energy content at room temperature and the associated density of states assures a good coupling between the pumped vibrational mode and the remaining modes which serve as an intramolecular heat bath. Facile multiphoton excitation results. In smaller molecules, however, multiphoton dissociation cross sections may be quite sensitive to the amount of internal energy present in the ions.[21, 29] It is for these smaller ions that infrared photochemical techniques are expected to yield the most information concerning energy disposal in ion-molecule reactions and vibrational energy relaxation mechanisms.

ACKNOWLEDGMENTS

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